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(54) Title: SUBSTITUTED PHENYL PYRIDAZINONES

(54) Rezeichnung: SUBSTITUIERTE PHENYLPYRIDAZINONE

(1)

(57) Abstract

The invention relates to novel substituted phenyl pyridazinones of formula (I), wherein R¹, R², R³, R⁴, R⁵ and R⁶ have the meanings cited in the description. The invention also relates to the production and use thereof as herbicides. The invention further relates to novel intermediate products.

Die Erfindung betrifft neue substituierte Phenylpyridazinone der allgemeinen Formel (I), in welcher R¹, R², R³, R⁴, R⁵ und R⁶ die in der Beschreibung gennanten Bedeutungen haben, Verfahren zu ihrer Herstellung, ihre Verwendung als Herbizide sowie neue Zwischenprodukte.

Substituted phenylpyridazinones

Abstract

The invention relates to novel substituted phenylpyridazinones of the general formula (I),

in which R1, R2, R3, R4, R5 and R6 are as defined in the description,

to processes for their preparation, to their use as herbicides and to novel intermediates.



Substituted phenylpyridazinones

The invention relates to novel substituted phenylpyridazinones, to processes for their preparation and to their use as crop protection agents, in particular as herbicides and as insecticides.

It is already known that certain substituted phenylpyridazinones have herbicidal properties (cf. DE-A-1105232, DE-A-1670309, DE-A-1670315, DE-A-1695840, DE-A-2526643, DE-A-2706700, DE-A-2808193, DE-A-2821809, DE-A-19754348, US-A-5298502, WO-A-96/39392, WO-A-97/07104). The herbicidal activity of these compounds is not entirely satisfactory.

This invention, accordingly, provides the novel substituted phenylpyridazinones of the general formula (I)

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in which

R1 represents hydrogen, fluorine, chlorine or bromine,

- R² represents cyano, carbamoyl, thiocarbamoyl, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted alkyl, alkoxy or alkylthio having in each case 1 or 2 carbon atoms,
- 25 R³ represents the grouping -A¹-A²-A³



in which

- A¹ represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, C₁-C₄-alkyl, C₃-C₄-alkenyl, C₃-C₄-alkinyl, C₁-C₄-alkoxy, phenyl, C₁-C₄-alkylsulphonyl or phenylsulphonyl,
- A¹ furthermore represents in each case optionally fluorine-, chlorine- or bromine-substituted C₁-C₆-alkanediyl, C₂-C₆-alkenediyl, C₂-C₆-azaalkenediyl, C₂-C₆-alkinediyl, C₃-C₆-cycloalkanediyl, C₃-C₆-cycloalkenediyl or phenylene,
 - A² represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, C₁-C₄-alkyl, C₁-C₄-alkoxy, phenyl, C₁-C₄-alkylsulphonyl or phenylsulphonyl,
 - A² furthermore represents in each case optionally fluorine-, chlorine-, bromine- or C₁-C₄-alkoxy-substituted C₁-C₆-alkanediyl, C₂-C₆-alkanediyl, C₂-C₆-azaalkenediyl, C₂-C₆-alkinediyl, C₃-C₆-cycloalkenediyl or phenylene,
 - A³ represents hydrogen, hydroxyl, amino, cyano, isocyano, thiocyanato, nitro, formyl, carboxyl, carbamoyl, thiocarbamoyl, sulpho, chlorosulphonyl, fluorine, chlorine, bromine, represents in each case optionally hydroxyl-, fluorine-, chlorine-, C₁-C₄-alkoxy-, C₁-C₄-alkyl-carbonyloxy- or C₁-C₄-alkoxy-carbonyloxy-substituted alkyl, alkoxy, alkylthio, alkylsulphinyl, alkylsulphonyl, alkylamino, dialkylamino, alkoxycarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl or dialkoxy(thio)phosphoryl having in each case 1 to 6 carbon atoms in the alkyl groups, represents in each case optionally fluorine- or chlorine-

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substituted alkenyl, alkenyloxy, alkenylamino, alkylideneamino, alkenyloxycarbonyl, alkinyloxy, alkinylamino or alkinyloxycarbonyl having in each case 2 to 6 carbon atoms in the alkenyl, alkylidene or alkinyl groups, represents in each case optionally fluorine-, chlorine-, cyano-, carboxyl-, C1-C4-alkyl- and/or C1-C4-alkoxy-carbonyl-substituted cycloalkyl, cycloalkyloxy, cycloalkylamino, cycloalkylalkyl, cycloalkylalkoxy, cycloalkylalkylamino, cycloalkylalkyl, cycloalkylalkoxy, cycloalkylalkylamino, cycloalkylideneamino, cycloalkyloxycarbonyl or cycloalkylalkoxy-carbonyl having in each case 3 to 6 carbon atoms in the cycloalkyl groups and optionally 1 to 4 carbon atoms in the alkyl groups, or represents in each case optionally nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, C1-C4-alkyl-, C1-C4-halogenoalkyl, C1-C4-alkyloxy, C1-C4-halogenoalkyloxy- and/or C1-C4-alkoxy-carbonyl-substituted phenyl, phenyloxy, phenyl-C1-C4-alkyl, phenyl-C1-C4-alkoxy, phenyloxycarbonyl or phenyl-C1-C4-alkoxycarbonyl,

A³ furthermore represents in each case optionally fully or partially hydrogenated pyrrolyl, pyrazolyl, imidazolyl, triazolyl, furyl, oxiranyl, oxetanyl, dioxolanyl, dioxanyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolyl-C₁-C₄-alkyl, furyl-C₁-C₄-alkyl, thienyl-C₁-C₄-alkyl, oxazolyl-C₁-C₄-alkyl, isoxazole-C₁-C₄-alkyl, thiazole-C₁-C₄-alkyl, pyridinyl-C₁-C₄-alkyl, pyrimidinyl-C₁-C₄-alkyl, pyrizolylmethoxy, furylmethoxy, represents perhydropyranylmethoxy or pyridylmethoxy,

R⁴

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represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally-fluorine- and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino, dialkylamino or alkoxycarbonyl having in each case 1 to 4 carbon atoms in the alkyl groups,



- R5 represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino, dialkylamino or alkoxycarbonyl having in each case 1 to 4 carbon atoms in the alkyl groups, and
- R6 represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino, dialkylamino or alkoxycarbonyl having in each case 1 to 4 carbon atoms in the alkyl groups.

The novel substituted phenylpyridazinones of the general formula (I) have interesting biological properties, in particular strong herbicidal and insecticidal activity.

In the definitions, the saturated or unsaturated hydrocarbon chains, such as alkyl, alkenyl or alkinyl, are in each case straight-chain or branched.

Halogen generally represents fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine, in particular fluorine or chlorine.

- R1 preferably represents hydrogen, fluorine or chlorine;
- R² preferably represents cyano, carbamoyl, thiocarbamoyl, fluorine, chlorine, bromine, methyl or trifluoromethyl;
 - R³ preferably represents the grouping -A¹-A²-A³

in which

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A¹ represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, methyl, ethyl, n- or i-propyl, methoxy, ethoxy, n- or i-propoxy, methylsulphonyl or ethylsulphonyl,

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Al furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, ethene-1,2-diyl, propene-1,2-diyl, propene-1,2-diyl, propene-1,2-diyl, propine-1,2-diyl, propine-1,3-diyl,

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A² represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, methyl, ethyl, n- or i-propyl, methoxy, ethoxy, n- or i-propoxy, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl or phenylsulphonyl,

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A² furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, ethene-1,2-diyl, propene-1,2-diyl, propene-1,2-diyl, propene-1,2-diyl, propine-1,2-diyl, propine-1,3-diyl,

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A³ represents hydrogen, hydroxyl, amino, cyano, nitro, formyl, carboxyl, carbamoyl, sulpho, fluorine, chlorine, bromine, represents in each case optionally fluorine-, chlorine-, methoxy- or ethoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-, i-, s- or t-pentyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, n-, i-, s- or t-pentyloxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylsulphinyl, ethylsulphinyl, n- or i-propylsulphinyl, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino, diethylamino, methoxycarbonyl, ethoxycarbonyl, n- or i-



propoxycarbonyl, dimethoxyphosphoryl, diethoxyphosphoryl or dipropoxyphosphoryl, diisopropoxyphosphoryl, represents in each case optionally fluorine- or chlorine- substituted ethenyl, propenyl, butenyl, propenyloxy, butenyloxy, propenylamino, butenylamino, propylideneamino, butylideneamino, propenyloxycarbonyl, butenyloxycarbonyl, ethinyl, propinyl, butinyl, propinyloxy, butinyloxy, propinylamino, butinylamino, propinyloxycarbonyl or butinyloxycarbonyl, represents in each case optionally fluorine-, chlorine-, cyano-, carboxyl-, methyl-, ethyl-, n- or i-propyl-, methoxycarbonyl- or ethoxycarbonylsubstituted cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, cyclopropylmethoxy, cyclobutylmethoxy, methoxy, cyclohexylmethoxy, cyclopentylideneamino, hexylideneamino, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, cyclopentylmethoxycarbonyl or cyclohexylmethoxycarbonyl, or represents in each case optionally nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy-, trifluoromethoxy-, methoxycarbonyl- and/or ethoxycarbonyl-substituted phenyl, phenyloxy, benzyl, phenylethyl, benzyloxy, phenyloxycarbonyl, benzyloxycarbonyl,

A³ furthermore represents (in each case optionally fully or partially hydrogenated) dioxolanyl, dioxanyl, pyrrolyl, pyrazolyl, imidazolyl, triazolyl, furyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolylmethyl, furylmethyl, thienylmethyl, oxazolylmethyl, isoxazolemethyl, thiazolemethyl, pyridinylmethyl, pyrimidinylmethyl, pyrazolylmethoxy, furylmethoxy or pyridylmethoxy;

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- R⁴ preferably represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino, dimethylamino, methoxycarbonyl or ethoxycarbonyl;
- R⁵ preferably represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino, dimethylamino, methoxycarbonyl or ethoxycarbonyl; and
- preferably represents hydrogen, carboxyl, cyano, carbamoyl, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine- and/or chlorine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino, dimethylamino, methoxycarbonyl or ethoxycarbonyl.
 - R¹ particularly preferably represents hydrogen, fluorine or chlorine;
- R² particularly preferably represents cyano or thiocarbamoyl;
 - R³ particularly preferably represents the grouping -A¹-A²-A³,
- 25 in which
 - A¹ represents a single bond, represents oxygen, sulphur, -SO₋, -SO₂₋, -CO₋ or the grouping -N-A⁴-, in which A⁴ represents hydrogen, methyl, ethyl, n- or i-propyl, methylsulphonyl or ethylsulphonyl,



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A¹ furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, ethene-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,

A² represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, methyl, ethyl, n- or i-propyl, methoxy, ethoxy, n- or i-propoxy, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl or phenylsulphonyl,

A² furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, ethene-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,

represents hydrogen, hydroxyl, amino, cyano, nitro, carboxyl, carbamoyl, sulpho, fluorine, chlorine, bromine, represents in each case optionally fluorine-, chlorine-, methoxy- or ethoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-, i-, s- or t-pentyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, n-, i-, s- or t-pentyloxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylsulphinyl, ethylsulphinyl, n- or i-propylsulphinyl, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino, diethylamino, methoxycarbonyl, ethoxycarbonyl, n- or ipropoxycarbonyl, represents in each case optionally fluorine- or chlorine-substituted propenyl, butenyl, propenyloxy, butenyloxy, propenylamino, butenylamino, propylideneamino, butylideneamino, propenyloxycarbonyl, butenyloxycarbonyl, propinyl, butinyl, propinyloxy, butinyloxy, propinylamino, butinylamino, propinyloxycarbonyl or butinyloxycarbonyl, represents in each case optionally fluorine-, chlorine-, cyano-, carboxyl-, methyl-, ethyl-, n- or i-propyl-, methoxy-

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A3

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carbonyl- or ethoxycarbonyl-substituted cyclopropyl, cyclobutyl, cyclopentyl, cyclopentyl, cyclopentyl, cyclopentyl, cyclopentyl, cyclopentyl-oxy, cyclohexyloxy, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclopentylmethyl, cyclopentylmethoxy, cyclopentylmethoxy, cyclopentylideneamino, cyclopentylmethoxy, cyclopentylideneamino, cyclopentylmethoxycarbonyl, cyclohexyloxycarbonyl, cyclopentylmethoxycarbonyl or cyclohexylmethoxycarbonyl, or represents in each case optionally nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy-, trifluoromethoxy-, methoxycarbonyl- and/or ethoxycarbonyl-substituted phenyl, phenyloxy, benzyl, phenylethyl, benzyl-oxy, phenyloxycarbonyl or benzyloxycarbonyl,

A³ furthermore represents pyrazolyl, imidazolyl, triazolyl, furyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolylmethyl, furylmethyl, thienylmethyl, oxazolylmethyl, isoxazolemethyl, thiazolemethyl, pyridinylmethyl, pyrimidinylmethyl, pyrazolylmethoxy, furylmethoxy or pyridylmethoxy;

R⁴ particularly preferably represents hydrogen, cyano, thiocarbamoyl, nitro, fluorine, chlorine, bromine, or represents in each case optionally fluorine-and/or chlorine- substituted methyl, ethyl, n- or i-propyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino or dimethylamino;

R5 particularly preferably represents in each case fluorine- and/or chlorinesubstituted methyl, ethyl, n- or i-propyl; and

particularly preferably represents hydrogen, cyano, thiocarbamoyl, nitro, fluorine, chlorine, bromine, or represents in each case optionally fluorine-

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R6



and/or chlorine-substituted methyl, ethyl, n- or i-propyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino, dimethylamino, methoxy-carbonyl or ethoxycarbonyl.

- The abovementioned general or preferred radical definitions apply both to the end products of the formula (I) and, correspondingly, to the starting materials or intermediates required in each case for the preparation. These radical definitions can be combined with one another as desired, i.e. including combinations between the given preferred ranges.
 - Preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being preferred.
- Particular preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being particularly preferred.

Very particularly preferred compounds of the formula (I) are listed in the groups below.

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Group 1

$$Ar - N = CF_3 \qquad (IA-1)$$

Ar has here, for example, the meanings listed below:

4-cyano-phenyl, 2-fluoro-4-cyano-phenyl, 2-chloro-4-cyano-phenyl, 3-fluoro-4-cyano-phenyl, 2-fluoro-5-chloro-4-cyano-phenyl, 2,5-dichloro-4-cyano-phenyl, 2-chloro-5-fluoro-4-cyano-phenyl, 2-chloro-4-fluoro-5-cyano-phenyl, 2,5-difluoro-4-cyano-phenyl, 2-chloro-4-fluoro-5-cyano-phenyl, 2,5-difluoro-4-cyano-phenyl, 2-chloro-4-



cyano-5-methyl-phenyl, 2-fluoro-4-cyano-5-methyl-phenyl, 2-chloro-4-cyano-5-trifluoromethyl-phenyl, 2-fluoro-4-cyano-5-trifluoromethyl-phenyl, 2,5-difluoro-4-thio-2-fluoro-4-cyano-5-methoxy-phenyl, carbamoyl-phenyl, 2-fluoro-4-cyano-5-ipro-poxy-phenyl, 2-chloro-4-cyano-5-(2-propinyloxy)-phenyl, 2-fluoro-4-cyano-5-(1methyl-2-propinyloxy)-phenyl, 2-chloro-4-thiocarbamoyl-5-i-propoxy-phenyl, 2-fluoro-4-cyano-5-(2-propenyloxy)-phenyl, 2-chloro-4-cyano-5-methylsulphonylamino-phenyl, 2-fluoro-4-cyano-5-ethylsulphonylamino-phenyl, 2-fluoro-4-thiocarbamoyl-5-methylsulphonylamino-phenyl, 2-chloro-4-cyano-5-ethylsulphonylamino-phenyl, 2-fluoro-4-cyano-5-cyclopropylsulphonylamino-phenyl, 2-fluoro-4-2-chloro-4-thiocarbamoyl-5-ethylcyano-5-i-propylsulphonylamino-phenyl, sulphonylamino-phenyl, 2-chloro-4-cyano-5-cyanamino-phenyl, 2-fluoro-4-cyano-5-2-fluoro-4-cyano-5-(2,2-difluoroethyltrifluoromethylsulphonylamino-phenyl, 2-fluoro-4-cyano-5-phenylsulphonylamino-phenyl, sulphonylamino)-phenyl, 2-chloro-4-cyano-5-methoxyfluoro-4-cvano-5-t-butylsulphonylamino-phenyl, 2-fluoro-4-thio-2-fluoro-4-cyano-5-ethoxycarbonyl-phenyl, carbonyl-phenyl, carbamoyl-5-methoxycarbonyl-phenyl, 2-fluoro-4-cyano-5-(1-methyl-2-propinylthio)-phenyl, 2-fluoro-4-cyano-5-methylamino-phenyl, 2-chloro-4-thiocarbamoyl-5methoxycarbonylmethyl-phenyl, 2-chloro-4-cyano-5-(N-methyl-ethylsulphonylamino)-phenyl, 2-chloro-4-cyano-5-i-propoxycarbonyl-phenyl, 2-fluoro-4-cyano-5-(bis-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-methylsulphonyl-N-ethylsulphonylamino)-phenyl, 2-fluoro-4-cyano-5-(1-methoxycarbonyl-ethoxy)-phenyl, 2fluoro-4-cyano-5-cyclopropyloxy-phenyl, 2-chloro-4-cyano-5-dimethylamino-phenyl, 2-fluoro-4-cyano-5-tetrahydrofurylmethoxy-phenyl, 2-fluoro-4-cyano-5-amino-2-fluoro-4-cyano-5-2-fluoro-4-cyano-5-methylaminocarbonyl-phenyl, methylsulphonyloxy-phenyl, 2-chloro-4-cyano-5-difluoromethoxy-phenyl, 2-fluoro-2-fluoro-4-cyano-5-dimethylamino-4-cyano-5-ethoxycarbonylmethoxy-phenyl, carbonyl-phenyl, 2-fluoro-4-cyano-5-cyanomethoxy-phenyl, 2-fluoro-4-cyano-5-(2-2-fluoro-4-cyano-5-hydroxy-phenyl, chloro-2-propenyloxy)-phenyl, 2-fluoro-4-cyano-5-diethoxyphosphorylamino-phenyl, cyano-5-nitro-phenyl, fluoro-4-cyano-5-chlorosulphonyl-phenyl, 2-fluoro-4-cyano-5-formylamino-phenyl, 2-fluoro-4-cyano-5-diethoxy-2-chloro-4-cyano-5-ethoxycarbonyloxy-phenyl,

PATER OFFICE

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phosphorylmethoxy-phenyl, 2-chloro-4-cyano-5-hydroxy-phenyl, 2-fluoro-4-cyano-5-(N,N-diacetyl-amino)-phenyl, 2-fluoro-4-cyano-5-acetylamino-phenyl, 2-chloro-4cyano-5-thiocyanato-phenyl, 2-fluoro-4-cyano-5-diethylaminooxy-phenyl, 2-fluoro-4-cyano-5-tetrahydrofuryloxy-phenyl, 2-fluoro-4-cyano-5-ureido-phenyl, 2-fluoro-4cyano-5-dimethoxymethyleneamino-phenyl, 2-chloro-4-cyano-5-ethoxymethyleneamino-phenyl, 2-fluoro-4-cyano-5-(2-chloro-ethoxycarbonyloxy)-phenyl, 2-chloro-4cyano-5-dimethylaminomethylenamino-phenyl, 2-chloro-4-cyano-5-(perhydropyran-4-yloxy)-phenyl, 2-fluoro-4-cyano-5-(2-methoxycarbonyl-ethyl)-phenyl, 2-chloro-4cyano-5-(2-carboxy-2-chloro-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-chioro-2methoxycarbonyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-s-butoxycarbonyl)phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-carbamoyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-methoxycarbonyl-1-methyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(1,2dibromo-2-methoxycarbonyl-ethyl)-phenyl, 2-chloro-4-cyano-5-(2-chloro-2-ipropoxy-carbonyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-carboxy-2-chloro-ethyl)phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-ethylaminocarbonyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-allylaminocarbonyl-2-chloro-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2ethoxycarbonyl-ethenyl)-phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-cyclopropylaminocarbonyl-ethyl)-phenyl, 2-fluoro-4-cyano-5-(2-chloro-2-dimethylaminocarbonylethyl)-phenyl, 2-chloro-4-cyano-5-(2-chloro-2-ethylsulphonylaminocarbonyl-ethyl)phenyl. 2-fluoro-4-thiocarbamoyl-5-(2-ethylaminocarbonyl-ethenyl)-phenyl, fluoro-4-cyano-5-(1-ethoxycarbonyl-ethyl)-phenyl, 2-chloro-4-cyano-5-(1-ethoxycarbonylethyl)-phenyl, 2-chloro-4-cyano-5-carboxy-phenyl, 2-fluoro-4-cyano-5-ibutoxy-phenyl, 2-chloro-4-cyano-5-i-butoxy-phenyl, 2-chloro-4-cyano-5-(2-methoxyethoxy)-phenyl, 2-fluoro-4-cyano-5-(N-acetyl-N-methylsulphonyl-amino)-phenyl, 2fluoro-4-cyano-5-(N-propionyl-N-methylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-i-butyroyl-N-methylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-pivaloyl-N-methylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-benzoyl-N-methylsulphonyl-amino)-phenyl, -2-fluoro-4-cyano-5-(N-(4-methoxy-benzoyl)-N-methylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-acetyl-N-ethylsulphonyl-amino)phenyl, 2-fluoro-4-cyano-5-(N-propionyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-i-butyroyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-

pivaloyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-cyano-5-(N-benzoyl-N-ethyl-2-fluoro-4-cyano-5-(N-(4-methoxy-benzoyl)-N-ethylsulphonyl-amino)-phenyl, sulphonyl-amino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-acetyl-N-methylsulphonylamino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-propionyl-N-methylsulphonylamino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-i-butyroyl-N-methylsulphonylamino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-pivaloyl-N-methylsulphonyl-amino)phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-benzoyl-N-methylsulphonyl-amino)-phenyl, 2-fluoro-4 thiocarbamoyl-5-(N-(4-methoxy-benzoyl)-N-methylsulphonyl-amino)phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-acetyl-N-ethylsulphonyl-amino)-phenyl, 2fluoro-4-thiocarbamoyl-5-(N-propionyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4thiocarbamoyl-5-(N-i-butyroyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-pivaloyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-benzoyl-N-ethylsulphonyl-amino)-phenyl, 2-fluoro-4-thiocarbamoyl-5-(N-(4-methoxy-benzoyl)-N-ethylsulphonyl-amino)-phenyl.

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Group 2

Ar has here, for example, the meanings listed above in Group 1.

20

Group 3

$$Ar-N$$
 CF_3
(IA-3)

Ar has here, for example, the meanings listed above in Group 1.



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Group 4

Ar has here, for example, the meanings listed above in Group 1.

Group 5

$$Ar - N \longrightarrow CF_3 \qquad (IA-5)$$

10 Ar has here, for example, the meanings listed above in Group 1.

Group 6

$$Ar-N$$
 CF_3 (IA-6)

15 Ar has here, for example, the meanings listed above in Group 1.

Group 7

$$Ar - N \longrightarrow CF_3$$

$$CF_3$$

$$(IA-7)$$



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Ar has here, for example, the meanings listed above in Group 1.

Group 8

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Ar has here, for example, the meanings listed above in Group 1.

Group 9

$$Ar - N = CF_3$$

$$CH_3$$

$$CH_3$$

$$(IA-9)$$

10

Ar has here, for example, the meanings listed above in Group 1.

Group 10

$$Ar - N \longrightarrow CH_3$$

$$-CF_3$$

$$(IA-10)$$

15

Ar has here, for example, the meanings listed above in Group 1.

Group 11



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Ar has here, for example, the meanings listed above in Group 1.

Group 12

 $Ar - N \longrightarrow CHF_2$ CHF_2 (IA-12)

5

Ar has here, for example, the meanings listed above in Group 1.

Group 13

Ar-N CH_3 CF_2CI CIA-13

10

Ar has here, for example, the meanings listed above in Group 1.

Group 14

Ar—N——CF₂CI

CH₃

(IA-14)

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Ar has here, for example, the meanings listed above in Group 1.

Group 15



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Ar has here, for example, the meanings listed above in Group 1.

5 <u>Group 16</u>

$$Ar-N$$
 CF_3
(IA-16)

Ar has here, for example, the meanings listed above in Group 1.

10 <u>Group 17</u>

Ar has here, for example, the meanings listed above in Group 1.

15 <u>Group 18</u>

Ar has here, for example, the meanings listed above in Group 1.



Group 19

$$Ar-N = CF_3$$

$$-CH_3 \qquad (IA-19)$$

Ar has here, for example, the meanings listed above in Group 1.

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Group 20

$$Ar - N = CH_3$$

$$CF_3$$

$$C_2H_5$$
(IA-20)

Ar has here, for example, the meanings listed above in Group 1.

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Group 21

$$Ar-N \xrightarrow{CH_3} CHF_2$$

$$CH_3 \qquad \qquad (IA-21)$$

Ar has here, for example, the meanings listed above in Group 1.

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Group 22

$$Ar - N - CH_3$$

$$CF_2CI$$

$$CH_3$$

$$CH_3$$

$$(IA-22)$$



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Ar has here, for example, the meanings listed above in Group 1.

Group 23

$$Ar-N = CH_3$$

$$C_2F_5$$

$$CH_3$$

$$CH_3$$

$$(IA-23)$$

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Ar has here, for example, the meanings listed above in Group 1.

Group 24

$$Ar - N = CH_3$$

$$CF_3$$

$$CF_3$$

$$(IA-24)$$

10

Ar has here, for example, the meanings listed above in Group 1.

Group 25

$$Ar - N - CF_3$$

$$C_2H_5$$
(IA-25)

15

Ar has here, for example, the meanings listed above in Group 1.

Group 26

$$Ar-N$$
 $COOC_2H_5$
 CF_3
 CH_3
(IA-26)



- 20 -

Ar has here, for example, the meanings listed above in Group 1.

5 <u>Group 27</u>

$$Ar - N = COOC_2H_5$$

$$CF_3$$
(IA-27)

Ar has here, for example, the meanings listed above in Group 1.

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Group 28

Ar—N COOH
$$CF_3$$

$$CH_3$$
(IA-28)

Ar has here, for example, the meanings listed above in Group 1.

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Group 29

$$Ar-N = CR$$

$$CF_3$$

$$CH_3$$

$$(IA-29)$$

Ar has here, for example, the meanings listed above in Group 1.



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Group 30

$$Ar-N$$
 CF_3
(IA-30)

Ar has here, for example, the meanings listed above in Group 1.

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Group 31

$$Ar - N - CSNH_{2}$$

$$CF_{3}$$

$$CH_{3}$$

$$(IA-31)$$

Ar has here, for example, the meanings listed above in Group 1.

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Group 32

$$\begin{array}{c} \text{CSNH}_2\\ \text{CF}_3 \end{array} \hspace{0.5cm} \text{(IA-32)}$$

Ar has here, for example, the meanings listed above in Group 1.

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The novel substituted phenylpyridazinones of the general formula (I) are obtained when

(a) halogenoarenes of the general formula (II)



- 22 -

$$X^1$$
 R^3
 (II)

in which

 $R^1,\,R^2$ and R^3 are as defined above and

5

X1 represents halogen

are reacted with pyridazinones of the general formula (III)

$$\mathbb{R}^{\frac{N}{2}} \longrightarrow \mathbb{N}_{\mathbb{N}}$$
 (III)

10 in which

R⁴, R⁵ and R⁶ are as defined above,

or with acid adducts or alkali metal salts of compounds of the formula (III)

15

if appropriate in the presence of a reaction auxiliary and if appropriate in the presence of a diluent,

or when

20

(b) arylhydrazines of the general formula (IV)



- 23 -

in which

 R^1 , R^2 and R^3 are as defined above

5

are reacted with B-trihalomethyl-enones of the general formula (V)

in which

- 10 R4, R5 and R6 are as defined above and
 - X² represents halogen,
- if appropriate in the presence of a reaction auxiliary and if appropriate in the presence of a diluent,

or when

. (c) hydrazonecarboxylic acids of the general formula (VI)

$$\begin{array}{c|c}
R^5 \\
N \\
R^4 \\
COOH
\end{array}$$
 $\begin{array}{c}
R^1 \\
R^2$
 $\begin{array}{c}
(VI) \\
R^3
\end{array}$



in which

 R^1, R^2, R^3, R^4, R^5 and R^6 are as defined above are condensed with ring-closure, i.e. reacted with a dehydrating agent,

or when

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(d) 2,4-disubstituted phenylpyridazinones of the general formula (Ia)

$$R^{5}$$
 R^{4}
 R^{4}
 R^{2}
 R^{2}
 R^{2}
 R^{3}
 R^{4}
 R^{2}

10 in which

 R^1 , R^2 , R^4 , R^5 and R^6 are as defined above

are nitrated, i.e. reacted with a nitrating agent,

15

or when

(e) hydrazonecarbonyl compounds of the general formula (VII)

20 in which

 R^1 , R^2 , R^3 , R^5 and R^6 are as defined above



are reacted with alkoxycarbonylmethylenephosphoranes of the general formula (VIII)

$$R^4$$
 $P(C_6H_5)_3$ (VIII)

in which

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- R4 is as defined above and
- R represents alkyl having 1 to 6 carbon atoms,
- or with trialkyl phosphonocarboxylates of the general formula (IX)

in which

R4 is as defined above and

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R represents alkyl having 1 to 6 carbon atoms,

in each case optionally in the presence of a reaction auxiliary and optionally in the presence of a diluent.

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The compounds of the general formula (I) can also be converted by other customary methods into other compounds of the general formula (I) according to the above definition, for example by nucleophilic substitution (e.g. R^3 : $F \rightarrow OH$, SH, NH_2 , OCH_3 , $NHSO_2CH_3$) or by further transformations of functional groups (e.g. R^2 : $F/CI/Br \rightarrow CN$, $CONH_2 \rightarrow CN$, $CN \rightarrow CSNH_2$, $NO_2 \rightarrow NH_2$; R^3 : $NO_2 \rightarrow NH_2$, $NH_2 \rightarrow F$, CI, Br, CN, $NHSO_2CH_3$, SO_2CI , $OCH_3 \rightarrow OH$, $OH \rightarrow OCH_2CH=CH_2$) of also the Preparation Examples.



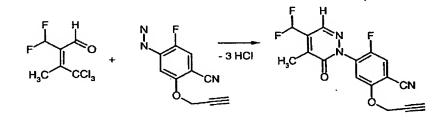
Using, for example, 4-fluoro-6-methyl-5-trifluoromethyl-pyridazin-3-one and 4,5-difluoro-2-methoxy-benzonitrile as starting materials, the course of the reaction in the process (a) according to the invention can be illustrated by the following formula scheme:

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$$F_3C$$
 CH_3
 F_3C
 N
 F_3C
 N
 F_3C
 N
 F
 CN
 OCH_3

Using, for example, 4,4,4-trichloro-3-methyl-2-difluoromethyl-crotonaldehyde and 4-cyano-2-fluoro-5-propargyloxy-phenylhydrazine as starting materials, the course of the reaction in the process (b) according to the invention can be illustrated by the following formula scheme:



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Using, for example, 2-chloro-3-chlorodifluoromethyl-4-oxo-2-butenoic acid N-(4-cyano-2-fluoro-5-methylsulphonylamino-phenyl)-hydrazone as starting material, the course of the reaction in the process (c) according to the invention can be illustrated by the following formula scheme:



Using, for example, 2-(2-chloro-4-cyano-phenyl)-4,6-dichloro-5-pentafluoroethylpyridazin-3-one and nitric acid as starting materials, the course of the reaction in the process (d) according to the invention can be illustrated by the following formula scheme:

Using, for example, 3,3,3-trifluoro-2-oxo-propanal 1-(4-cyano-2,5-difluorophenylhydrazone) and ethyl triphenylphosphoranylidene-acetate as starting materials, the course of the reaction in the process (e) according to the invention can be illustrated by the following formula scheme:

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The formula (II) provides a general definition of the halogenoarenes to be used as starting materials in the process (a) according to the invention for preparing the



compounds of the formula (I). In the formula (II), R¹, R² and R³ preferably or in particular have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred or as being particularly preferred for R¹, R² and R³; X¹ preferably represents fluorine, chlorine or bromine, in particular fluorine.

The starting materials of the formula (II) are known and/or can be prepared by processes known per se (cf. EP 191181, EP 370332, EP 431373, EP 441004).

The formula (III) provides a general definition of the pyridazinones further to be used as starting materials in the process (a) according to the invention. In the formula (III), R⁴, R⁵ and R⁶ preferably have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred, particularly preferred or very particularly preferred for R⁴, R⁵ and R⁶.

The starting materials of the formula (III) are known and/or can be prepared by processes known per se (cf. J. Chem. Soc. 1947, 239; Angew. Chem. 77 (1965), 282; Monatsh. Chem. 120 (1989), 329).

The formula (IV) provides a general definition of the arylhydrazines to be used as starting materials in the process (b) according to the invention for preparing the compounds of the formula (I). In the formula (IV), R^1 , R^2 and R^3 preferably have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred, particularly preferred or very particularly preferred for R^1 , R^2 and R^3 .

The starting materials of the formula (IV) are known and/or can be prepared by processes known per se (cf. EP 370332).



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The formula (V) provides a general definition of the β-trihalogenomethyl-enones further to be used as starting materials in the process (b) according to the invention. In the formula (V), R⁴, R⁵ and R⁶ preferably have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred, particularly preferred or very particularly preferred for R⁴, R⁵ and R⁶; X² preferably represents fluorine, chlorine or bromine, in particular chlorine.

The starting materials of the formula (V) are known and/or can be prepared by processes known per se (cf. DE 2706700).

The formula (VI) provides a general definition of the hydrazonecarboxylic acids to be used as starting materials in the process (c) according to the invention for preparing the compounds of the formula (I). In the formula (VI), R^1 , R^2 , R^3 , R^4 , R^5 and R^6 preferably have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred, particularly preferred or very particularly preferred for R^1 , R^2 , R^3 , R^4 , R^5 and R^6 .

The starting materials of the formula (VI) are known and/or can be prepared by processes known per se (cf. WO 9639392).

The hydrazonecarboxylic acids of the general formula (VI) are obtained when arythydrazines of the general formula (IV)

$$\begin{array}{ccc} NH_2 & R^1 \\ HN & & & \\ & & & \\ - & & & \\ & & & \\ & & & \\ \end{array}$$

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in which



R1, R2 and R3 are as defined above

are reacted with β-carboxy-enones of the general formula (X)

5 in which

R4, R5 and R6 are as defined above,

if appropriate in the presence of a diluent, such as, for example, ethanol, and if appropriate in the presence of a reaction auxiliary, such as, for example, p-toluenesulphonic acid, at temperatures between 0°C and 100°C.

The formula (Ia) provides a general definition of the 2,4-disubstituted phenyl-pyridazinones to be used as starting materials in the process (d) according to the invention for preparing compounds of the formula (I). In the formula (Ia), R¹, R², R⁴, R⁵ and R⁶ preferably have that meaning which has already been mentioned above, in the description of the compounds of the formula (I) to be prepared according to the invention, as being preferred, particularly preferred or very particularly preferred for R¹, R², R⁴, R⁵ and R⁶.

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The starting materials of the formula (Ia) are known and/or can be prepared by processes known per se (cf. the processes (a) to (c) according to the invention).

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The formula (VII) provides a general definition of the hydrazonecarbonyl compounds to be used as starting materials in the process (e) according to the invention for preparing compounds of the formula (I). In the formula (VII), R¹, R², R³, R⁵ and R⁶ preferably or in particular have those meanings which have already been mentioned above, in connection with the description of the compounds of the formula (I)



according to the invention, as being preferred, particularly preferred or very particularly preferred for R^1 , R^2 , R^3 , R^5 and R^6 .

The starting materials of the formula (VII) are known and/or can be prepared by processes known per se (cf. WO 9707104).

Not yet known from the literature and, as novel compounds, part of the subjectmatter of the present application, are the hydrazonecarbonyl compounds of the general formula (VIIa)

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in which

- R1 represents fluorine, chlorine or bromine,
- 15 R²⁻¹ represents cyano, carbamoyl, thiocarbamoyl, or represents in each case optionally fluorine- and/or chlorine-substituted alkyl, alkoxy or alkylthio having in each case 1 or 2 carbon atoms,
 - R^3 represents the grouping $-A^1-A^2-A^3$.

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in which

Al represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, C₁-C₄-alkyl, C₃-C₄-alkenyl, C₃-C₄-alkinyl, C₁-C₄-alkoxy, phenyl, C₁-C₄-alkylsulphonyl or phenylsulphonyl,



A¹ furthermore represents in each case optionally fluorine-, chlorine- or bromine-substituted C₁-C₆-alkanediyl, C₂-C₆-alkenediyl, C₂-C₆-azaalkenediyl, C₂-C₆-alkinediyl, C₃-C₆-cycloalkanediyl, C₃-C₆-cycloalkenediyl or phenylene,

A² represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, hydroxyl, C₁-C₄-alkyl, C₁-C₄-alkoxy, phenyl, C₁-C₄-alkylsulphonyl or phenylsulphonyl,

A² furthermore represents in each case optionally fluorine-, chlorine- or bromine-substituted C₁-C₆-alkanediyl, C₂-C₆-alkenediyl, C₂-C₆-azaalkenediyl, C₂-C₆-alkinediyl, C₃-C₆-cycloalkanediyl, C₃-C₆-cycloalkenediyl or phenylene,

 A^3 represents hydrogen, hydroxyl, amino, cyano, isocyano, thiocyanato, nitro, carboxyl, carbamoyl, thiocarbamoyl, sulpho, chlorosulphonyl, fluorine, chlorine, bromine, represents in each case optionally fluorine-, chlorine- or C1-C4-alkoxy-substituted alkyl, alkoxy, alkylthio, alkylsulphinyl, alkylsulphonyl, alkylamino, dialkylamino, alkoxycarbonyl or dialkoxy(thio)phosphoryl having in each case 1 to 6 carbon atoms in the alkyl groups, represents in each case optionally fluorine- or chlorine-substituted alkenyl, alkenyloxy, alkenylamino, alkylideneamino, alkenyloxycarbonyl, alkinyl, alkinyloxy, alkinylamino or alkinyloxycarbonyl having in each case 2 to 6 carbon atoms in the alkenyl, alkylidene or alkinyl groups, represents in each case optionally fluorine-, chlorine-, cyano-, carboxyl-, C1-C4-alkyl- and/or C1-C4-alkoxy-carbonyl-substituted cycloalkyl, cycloalkyloxy, cycloalkylalkyl, cycloalkylalkoxy, cycloalkylideneamino, cycloalkyloxycarbonyl or cycloalkylalkoxycarbonyl having in each case 3 to 6

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carbon atoms in the cycloalkyl groups and optionally 1 to 4 carbon atoms in the alkyl groups, or represents in each case optionally nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, C_1 - C_4 -alkyl-, C_1 - C_4 -halogenoalkyl-, C_1 - C_4 -alkyloxy-, C_1 - C_4 -halogenoalkyloxy-and/or C_1 - C_4 -alkoxy-carbonyl-substituted phenyl, phenyloxy, phenyl- C_1 - C_4 -alkyl, phenyl- C_1 - C_4 -alkoxy, phenyloxycarbonyl or phenyl- C_1 - C_4 -alkoxycarbonyl,

A³ furthermore represents in each case optionally fully or partially hydrogenated pyrrolyl, pyrazolyl, imidazolyl, triazolyl, furyl, oxiranyl, oxetanyl, dioxolanyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolyl-C₁-C₄-alkyl, furyl-C₁-C₄-alkyl, thienyl-C₁-C₄-alkyl, oxazolyl-C₁-C₄-alkyl, isoxazole-C₁-C₄-alkyl, thiazole-C₁-C₄-alkyl, pyridinyl-C₁-C₄-alkyl, pyriazolylmethoxy, furyl-

R⁵ represents hydrogen, cyano, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine-and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino or dialkylamino having in each case 1 to 4 carbon atoms in the alkyl groups, and

methoxy, represents perhydropyranylmethoxy or pyridylmethoxy,

R6 represents hydrogen, cyano, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case optionally fluorine-and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino or dialkylamino having in each case 1 to 4 carbon atoms in the alkyl groups.

The novel hydrazonecarbonyl compounds of the general formula (VIIa) are obtained when

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(a) arythydrazines of the general formula (IVa)



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$$\begin{array}{ccc} NH_2 & R^1 \\ HN & & \\ & & \\ R^3 & & \end{array}$$
 (IVa)

in which

5

 R^1 , R^{2-1} and R^3 are as defined above

are reacted with α-dihalogeno-carbonyl compounds of the general formula (XI)

$$R^{5} \xrightarrow{X^{3}} X^{3} \qquad (XI)$$

in which

- 10 R⁵ and R⁶ are as defined above and
 - x3 represents halogen (in particular chlorine or bromine),
- if appropriate in the presence of a diluent, such as, for example, water, and if appropriate in the presence of a reaction auxiliary, such as, for example, sodium acetate, at temperatures between 0°C and 100°C (cf. the Preparation Examples),

or when - in the case that R^6 represents hydrogen -

20 (β) arylamines of the general formula (XII)

$$H_2N$$
 R^3
 R^{2-1}
(XII)



in which

R^1 , R^{2-1} and R^3 are as defined above

are diazotized in a customary manner (for example by reaction with sodium nitrite and hydrochloric acid and/or acetic acid), the resulting diazonium compounds are reacted in a customary manner with 1,3-dicarbonyl compounds of the general formula (XIII)

- 10 in which
 - R⁵ is as defined above and
 - R represents alkyl (preferably methyl or ethyl)

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and the resulting compounds of the general formula (XIV)

$$R^{5}$$
 HN
 R^{1}
 R^{2-1}
 R^{2-1}
 R^{2-1}

in which

20 R, R^1 , R^{2-1} , R^3 and R^5 are as defined above

are hydrolyzed and decarboxylated in a customary manner.

The formulae (VIII) and (IX) provide general definitions of the alkoxycarbonylmethylenephosphoranes and trialkyl phosphonocarboxylates,

respectively, furthermore required as starting materials in the process (e) according to the invention for preparing compounds of the formula (I). In the formulae (VIII) and (IX), R⁴ in each case preferably has that meaning which has already been mentioned above, in connection with the description of the compounds of the formula (I) according to the invention, as being preferred, particularly preferred or very particularly preferred for R⁴; R in each case preferably represents alkyl having 1 to 4 carbon atoms, in particular methyl or ethyl.

The starting materials of the formulae (VIII) and (IX) are known chemicals for synthesis.

The processes (a), (b), (c), (d) and (e) according to the invention for preparing the compounds of the formula (I) are preferably carried out in the presence of a diluent. Suitable diluents are, in general, the customary organic solvents. These preferably include aliphatic, alicyclic and aromatic, optionally halogenated hydrocarbons, such as, for example, pentane, hexane, heptane, petroleum ether, ligroin, benzine, benzene, toluene, xylene, chlorobenzene, dichlorobenzene, cyclohexane, methylcyclohexane, dichloromethane (methylene chloride), trichloromethane (chloroform) or carbon tetrachloride, dialkyl ethers, such as, for example, diethyl ether, diisopropyl ether, methyl t-butyl ether, ethyl t-butyl ether, methyl t-pentyl ether (MTBE), ethyl t-pentyl ether, tetrahydrofuran (THF), 1,4-dioxane, ethylene glycol dimethyl ether or ethylene glycol diethyl ether, diethylene glycol dimethyl ether or diethylene glycol diethyl ether, dialkyl ketones, such as, for example, acetone, butanone (methyl ethyl ketone), methyl i-propyl ketone or methyl i-butyl ketone, nitriles, such as, for example, acetonitrile, propionitrile, butyronitrile or benzonitrile; amides, such as, for example, N,N-dimethyl-formamide (DMF), N,N-dimethyl-acetamide, N-methyl-formanilide, N-methyl-pyrrolidone or hexamethyl-phosphoric triamide; esters, such as, for example, methyl acetate, ethyl acetate, -n- or -i-propyl acetate, -n-, -i- or -s-butyl acetate; sulphoxides, such as, for example, dimethyl sulphoxide; alkanols, such as, for example, methanol, ethanol, n- or i-propanol, n-, i-, s- or t-butanol, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, diethylene glycol



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monomethyl ether or diethylene glycol monoethyl ether, mixtures thereof with water or pure water. In the process (b) according to the invention it is advantageously also possible to use acetic acid as diluent.

The processes (a), (b) and (e) according to the invention for preparing the compounds of the formula (I) are preferably carried out in the presence of a suitable reaction auxiliary. Suitable reaction auxiliaries are, in general, the customary inorganic or organic bases or acid acceptors. These preferably include alkali metal or alkaline earth metal acetates, amides, carbonates, bicarbonates, hydrides, hydroxides or alkoxides, such as, for example, sodium acetate, potassium acetate or calcium acetate, lithium amide, sodium amide, potassium amide or calcium amide, sodium carbonate, potassium carbonate or calcium carbonate, sodium bicarbonate, potassium bicarbonate or calcium bicarbonate, lithium hydride, sodium hydride, potassium hydride or calcium hydride, lithium hydroxide, sodium hydroxide, potassium hydroxide or calcium hydroxide, sodium methoxide, ethoxide, n- or i-propoxide, n-, i-, s- or t-butoxide or potassium methoxide, ethoxide, n- or i-propoxide, n-, i-, s- or tbutoxide; furthermore also basic organic nitrogen compounds, such as, for example, trimethylamine, triethylamine, tripropylamine, tributylamine, ethyl-diisopropylamine, N,N-dimethyl-cyclohexylamine, dicyclohexylamine, ethyl-dicyclohexylamine, N,Ndimethyl-aniline, N,N-dimethyl-benzylamine, pyridine, 2-methyl-, 3-methyl-, 4methyl-, 2,4-dimethyl-, 2,6-dimethyl-, 3,4-dimethyl- and 3,5-dimethyl-pyridine, 5ethyl-2-methyl-pyridine, 4-dimethylamino-pyridine, N-methyl-piperidine, 1,4-diazabicyclo[2,2,2]-octane (DABCO), 1,5-diazabicyclo[4,3,0]-non-5-ene (DBN), and 1,8-diazabicyclo[5,4,0]-undec-7-ene (DBU).

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The process (c) according to the invention for preparing the compounds of the formula (I) is carried out in the presence of a dehydrating agent. Suitable dehydrating agents are the customary dehydrating agents, such as, for example, sulphuric acid, methanesulphonic acid, benzenesulphonic acid, p-toluenesulphonic acid, acetic anhydride and phosphorus (V) oxide.



The process (d) according to the invention for preparing the compounds of the formula (I) is carried out using a nitrating agent. Suitable nitrating agents are the customary nitrating agents, such as, for example, nitric acid and its mixtures with nitrating auxiliaries, such as, for example, sulphuric acid.

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When carrying out the processes (a), (b), (c), (d) and (e) according to the invention, the reaction temperatures can be varied within a relatively wide range. In general, the processes are carried out at temperatures between -20°C and +200°C, preferably between 0°C and 150°C, in particular between 10°C and 120°C.

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The processes according to the invention are generally carried out under atmospheric pressure. However, it is also possible to carry out the processes according to the invention under elevated or reduced pressure - in general between 0.1 bar and 10 bar.

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For carrying out the processes (a), (b), (c), (d) and (e) according to the invention, the starting materials are generally employed in approximately equimolar amounts. However, it is also possible to use a relatively large excess of one of the components. The reaction is generally carried out in a suitable diluent, if appropriate in the presence of a reaction auxiliary, and the reaction mixture is generally stirred at the required temperature for several hours. Work-up is carried out by customary methods (cf. the Preparation Examples).

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The active compounds according to the invention can be used as defoliants, desiccants, haulm killers and, especially, as weed killers. By weeds in the broadest sense there are to be understood all plants which grow in locations where they are undesired. Whether the substances according to the invention act as total or selective herbicides depends essentially on the amount used. The active compounds according to the invention can be used, for example, in connection with the following plants:

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<u>Dicotyledonous weeds of the genera:</u> Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus,



Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea, Trifolium, Ranunculus, Taraxacum.

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<u>Dicotyledonous crops of the genera:</u> Gossypium, Glycine, Beta, Daucus, Phaseolus, Pisum, Solanum, Linum, Ipomoea, Vicia, Nicotiana, Lycopersicon, Arachis, Brassica, Lactuca, Cucumis, Cucurbita.

Monocotyledonous weeds of the genera: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus, Apera.

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Monocotyledonous crops of the genera: Oryza, Zea, Triticum, Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus, Allium.

However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other plants.

Depending on the concentration, the compounds are suitable for total weed control, for example on industrial terrain and rail tracks and on paths and areas with or without tree growth. Equally, the compounds can be employed for controlling weeds in perennial crops, for example forests, ornamental tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm plantations, cocoa plantations, soft fruit plantings and hop fields, on lawns and turf and pastures and for selective weed control in annual crops.

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The compounds of the formula (I) according to the invention have strong herbicidal activity and a broad activity spectrum when applied to the soil and to above-ground parts of plants.

The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders, granules, suspo-emulsion concentrates, natural and synthetic substances impregnated with active compound, and microencapsulations in polymeric substances.

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These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is to say liquid solvents and/or solid carriers, optionally with the use of surfactants, that is to say emulsifiers and/or dispersants and/or foam formers.

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If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Liquid solvents which are mainly suitable are: aromatics, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example petroleum fractions, mineral and vegetable oils, alcohols, such as butanol or glycol, and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and water.

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Suitable solid carriers are: for example ammonium salts and ground natural minerals, such as kaolins, clays, tale, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks, such as calcite, marble, pumice, sepiolite, dolomite and synthetic granules of inorganic and organic meals, and granules of organic



material, such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and protein hydrolysates; suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

Tackifiers, such as carboxymethylcellulose, natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, and also natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants, such as inorganic pigments, for example iron oxide, titanium oxide, Prussian blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

For controlling weeds, the active compounds according to the invention, as such or in the form of their formulations, can also be used as mixtures with known herbicides, finished formulations or tank mixes being possible.

Possible components for the mixtures are known herbicides, for example

acetochlor, acifluorfen(-sodium), aclonifen, alachlor, alloxydim(-sodium), ametryne, amidochlor, amidosulphuron, anilofos, asulam, atrazine, azafenidin, azimsulphuron, benazolin(-ethyl), benfuresate, bensulphuron(-methyl), bentazone, benzofenap, benzoylprop(-ethyl), bialaphos, bifenox, bispyribac(-sodium), bromobutide,

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bromofenoxim, bromoxynil, butachlor, butroxydim, butylate, cafenstrole, caloxydim, carbetamide, carfentrazone(-ethyl), chlomethoxyfen, chloramben, chloridazon, chlorimuron(-ethyl), chlornitrofen, chlorsulphuron, chlortoluron, cinidon(-ethyl), cinmethylin, cinosulphuron, clethodim, clodinafop(-propargyl), clomazone, clomeprop, clopyralid, clopyrasulphuron(-methyl), cloransulam(-methyl), cumyluron, cyanazine, cybutryne, cycloate, cyclosulphamuron, cycloxydim, cyhalofop(-butyl), 2,4-D, 2,4-DB, 2,4-DP, desmedipham, diallate, dicamba, diclofop(-methyl), diclosulam, diethatyl(-ethyl), difenzoquat, diflufenican, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimexyflam, dinitramine, diphenamid, diquat, dithiopyr, diuron, dymron, epoprodan, EPTC, esprocarb, ethalfluralin, ethametsulphuron(-methyl), ethofumesate, ethoxyfen, ethoxysulphuron, etobenzanid. fenoxaprop(-P-ethyl), flamprop(-isopropyl), flamprop(-isopropyl-L), flamprop(-methyl), flazasulphuron, fluazifop(-P-butyl), fluazolate, flucarbazone, flufenacet, flumetsulam, flumiclorac(-pentyl), flumioxazin, flumipropyn, flumetsulam, fluometuron, fluorochloridone, fluoroglycofen(-ethyl), flupropacil, flurpyrsulphuron(-methyl, -sodium), flurenol(-butyl), flupoxam, fluridone, fluroxypyr(-meptyl), flurprimidol, flurtamone, fluthiacet(-methyl), fluthiamide, fomesafen, glufosinate(-ammonium), glyphosate(-isopropylammonium), halosafen, haloxyfop(-ethoxyethyl), haloxyfop(-P-methyl), hexazinone. imazamethabenz(-methyl), imazamethapyr, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulphuron, iodosulphron, ioxynil, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxaflutole, isoxapyrifop, lactofen, lenacil, linuron, MCPA, MCPP, mefenacet, mesotrione, metamitron, metazachlor, methabenzthiazuron, metobenzuron, metobromuron, (alpha-)metolachlor, metosulam, metoxuron, metribuzin, metsulphuron(-methyl), molinate, monolinuron, naproanilide, napropamide, neburon, nicosulphuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulphuron, oxaziclomefone, oxyfluorfen, paraquat, pelargonic acid, pendimethalin, pentoxazone, phenmedipham, piperophos, pretilachlor, primisulphuron(-methyl), prometryn, propachlor, propaguizafop, propisochlor, propyzamide, prosulphuron, prosulphocarb, pyraflufen(-ethyl), pyrazolate, pyrazosulphuron(-ethyl), pyrazoxyfen, pyribenzoxim,



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pyributicarb, pyridate, pyriminobac(-methyl), pyrithiobac(-sodium), quinchlorac, quinmerac, quinoclamine, quizalofop(-P-ethyl), quizalofop(-P-tefuryl), rimsulphuron, sethoxydim, simazine, simetryn, sulcotrione, sulphentrazone, sulphometuron(-methyl), sulphosate, sulphosulphuron, tebuthiuron, tepraloxydim, terbuthylazine, terbutryn, thenylchlor, thiafluamide, thiazopyr, thidiazimin, thifensulphuron(-methyl), thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulphuron, tribenuron(-methyl), triclopyr, tridiphane, trifluralin triflusulphuron.

10 A mixture with other known active compounds, such as fungicides, insecticides, acaricides, nematicides, bird repellents, plant nutrients and agents which improve soil structure, is also possible.

The active compounds can be used as such, in the form of their formulations or in the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspensions, emulsions, powders, pastes and granules. They are used in the customary manner, for example by watering, spraying, atomizing, scattering.

The active compounds according to the invention can be applied both before and after emergence of the plants. They can also be incorporated into the soil before sowing.

The amount of active compound used can vary within a relatively wide range. It depends essentially on the nature of the desired effect. In general, the amounts used are between 1 g and 10 kg of active compound per hectare of soil surface, preferably between 5 g and 5 kg per ha.

The preparation and the use of the active compounds according to the invention can be seen from the examples below.

Preparation Examples:

Example 1

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5.0 g (18 mmol) of 3,3,3-trifluoro-2-oxo-propanal-1-(2,5-difluoro-4-cyano-phenyl-hydrazone) in 150 ml of toluene are admixed with 8.7 g (26 mmol) of methyl (triphenylphosphoranylidene)acetate, and the mixture is stirred at reflux temperature for 3 hours. The mixture is concentrated using a rotary evaporator, and the residue is recrystallized from isopropanol.

This gives 1.3 g (24% of theory) of 2-(2,5-difluoro-4-cyano-phenyl)-5-trifluoro-methyl-pyridazin-3-one of melting point 143°C.

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Example 2

5.0 g (18 mmol) of 3,3,3-trifluoro-2-oxopropanal-1-(2,5-difluoro-4-cyano-phenylhydrazone) in 150 ml of toluene are admixed with 9.4 g (26 mmol) of (1-ethoxycarbonylethylidene)triphenylphosphorane, and the mixture is stirred at reflux
rumperature for 3 hours. The mixture is concentrated using a rotary evaporator and
the residue is recrystallized from isopropanol.

This gives 2.41 g (42.5% of theory) of 2-(2,5-difluoro-4-cyano-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 135°C.

Analogously to Example 1 and 2, and in accordance with the general description of the preparation processes according to the invention, it is also possible to prepare the compounds of the formula (I) listed in Table 1 below.

Table 1: Examples of the compounds of the formula (I)

Ex.						
No.	R¹	R²	R³	R⁴	R ⁵	R ⁶
3	F	CN	NO ₂	Н	CF ₃	н
4	Cl	CN	NO₂	Н	CF ₃	Н
5	F	CN	NO₂	Н	CF ₃	CH ₃
6	Cl	CN	NO ₂	Н	CF ₃	CH ₃
7	F	CN	NO₂	CH ₃	CF ₃	Н
8	Cl	CN	NO ₂	CH ₃	CF ₃	Н
9	Cl	CN	ОН	Н	CF ₃	Н
10	F	CN	ОН	CH ₃	CF ₃	Н
11	F	CN	OCH ₃	CH ₃	CF ₃	Н
12	F	CN	OC ₂ H ₅	CH ₃	CF ₃	Н
13	F	CN	OCH(CH ₃) ₂	CH ₃	CF ₃	Н

Ex.		-				
No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
14	F	CN	OCH ₂ CH=CH ₂	CH ₃	CF ₃	Н
15	F	CN	OCH2C≡CH	CH ₃	CF ₃	H
16	F	CN	OCH(CH₃)C≡CH	CH ₃	CF ₃	Н
17	F	CN	OCH₂COOCH₃	CH ₃	CF ₃	Н
18	F	CN	OCH ₂ COOC ₂ H ₅	CH ₃	CF ₃	H
19	F	CN	OCH ₂ COOCH(CH ₃) ₂	CH ₃	CF ₃	Н
20	F	CN	OCH2COOC5H11	CH ₃	CF ₃	Н
21	F	CN	OCH(CH₃)COOC₂H₅	CH ₃	CF ₃	H
22	F	CN	ОН	Н	CF ₃	Н
23	F	CN	OCH ₃	Н	CF ₃	H
24	F	CN	OC ₂ H ₅	Н	CF ₃	H
25	F	CN	OCH(CH ₃) ₂	Н	CF ₃	H
26	F	CN	OCH ₂ CH=CH ₂	Н	CF ₃	H
27	F	CN	OCH₂C ≡ CH	Н	CF ₃	H
28	F	CN	OCH(CH₃)C≡CH	Н	CF ₃	Н
29	F	CN	OCH₂COOCH₃	Н	CF ₃	H
30	F	CN	OCH ₂ COOC ₂ H ₅	Н	CF ₃	Н
31	F	CN	OCH ₂ COOCH(CH ₃) ₂	Н	CF ₃	H
32	F	CN	OCH2COOC5H11	Н	CF ₃	Н
33	F	CN	OCH(CH ₃)COOC ₂ H ₅	Н	CF ₃	Н
34	F	CN	COOC ₂ H ₅	CH ₃	CF ₃	H .
35	F	CN	COOC₂H₅	Н	CF ₃	Н
36	F	CN	CONHCH ₃	CH ₃	CF ₃	Н
37	F	CN	CON(CH ₃) ₂	CH ₃	CF ₃	H
38	F	CN	NH ₂	CH ₃	CF ₃	Н
39	F	CN	NH ₂	Н	CF ₃	Н
40	F	CN	NHSO ₂ CH ₃	CH ₃	CF ₃	Н



Ex.						
No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
41	F	CN	NHSO ₂ C ₂ H ₅	CH ₃	CF ₃	Н
42	F	CN	NHSO ₂ CH ₂ Cl	CH ₃	CF ₃	н
43	F	CN	NHSO ₂ CF ₃	CH ₃	CF ₃	H
44	F	CN	NHSO ₂ cyclopropyl	CH ₃	CF ₃	Н
45	F	CN	NHSO ₂ CH ₃	Н	CF ₃	Н
46	F,	CN	NHSO ₂ C ₂ H ₅	H	CF ₃	Н
47	F	CN	NHSO ₂ CH ₂ Cl	Н	CF ₃	Н
48	F	CN	NHSO ₂ CF ₃	н	CF ₃	Н
49	F	CN	NHSO ₂ cyclopropyl	Н	CF ₃	Н
50	Cì	CN	NH ₂	Н	CF ₃	Н
51	Cl	CN	OCH2C≡CH	Н	CF ₃	Н
52	Cl	CN	OCH(CH ₃)C≡CH	Н	CF ₃	Н
53	Cl	CN	OCH ₂ COOCH ₃	Н	CF ₃	Н
54	Cl	CN	OCH2COOC2H5	Н	CF ₃	н
55	Cl	CN	OCH ₂ COOCH(CH ₃) ₂	Н	CF ₃	Н
56	Cl	CN	OCH2COOC5H11	Н	CF ₃	Н
57	Cl	CN	NHSO ₂ CH ₃	CH ₃	CF ₃	Н
58	Cl	CN	NHSO ₂ C ₂ H ₅	CH ₃	CF ₃	Н
59	Cl	CN	OCH ₂ C≡CH	CH ₃	CF ₃	Н
60	Cl	CN	OCH(CH ₃)C≡CH	CH ₃	CF ₃	Н
61	Cl	CN	OCH ₂ COOCH ₃	CH ₃	CF ₃	Н
62	Cl	CN	OCH ₂ COOC ₂ H ₅	CH ₃	CF ₃	Н
63	Cl	CN	OCH ₂ COOCH(CH ₃) ₂	CH ₃	CF ₃	Н
64	Cl	CN	OCH ₂ COOC ₅ H ₁₁	CH ₃	CF ₃	Н
65	F	CSNH ₂	NHSO ₂ CH ₃	CH ₃	CF ₃	Н
66	F	CSNH ₂	NHSO ₂ C ₂ H ₅	CH ₃	CF ₃	Н
67	F	CSNH ₂	NHSO ₂ CH ₃	Н	CF ₃	Н
						

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Ex.						
No.	R¹	R²	R³	R ⁴	R ⁵	R ⁶
68	F	CSNH ₂	NHSO ₂ C ₂ H ₅	Н	CF ₃	Н
69	Cl	CSNH ₂	OCH(CH₃)C≡CH	CH ₃	CF ₃	Н
70	Cl	CSNH ₂	OCH ₂ COOC ₅ H ₁₁	CH ₃	CF ₃	Н
71	F	CSNH ₂	OCH ₂ CH=CH ₂	н	CF ₃	Н
72	F	CSNH₂	OCH ₂ C≡CH	Н	CF ₃	Н
73	F	CSNH ₂	OCH(CH ₃)C≡CH	Н	CF ₃	Н
74	Ci ·	CSNH ₂	NHSO ₂ CH ₃	Н	CF ₃	Н
75	Cl	CSNH ₂	NHSO ₂ C ₂ H ₅	Н	CF ₃	Н
76	F	CSNH ₂	OCH ₂ CH=CH ₂	CH ₃	CF ₃	Н
77	F	CSNH ₂	OCH ₂ C≡CH	CH ₃	CF ₃	Н
78	F	CSNH ₂	OCH(CH ₃)C≡CH	CH ₃	CF ₃	Н
79	Cl	CSNH ₂	NHSO ₂ CH ₃	CH ₃	CF ₃	Н
80	Cl	CSNH ₂	NHSO₂C₂H₅	CH ₃	CF ₃	Н
81	F	CN	N(SO ₂ CH ₃) ₂	CH ₃	CF ₃	Н
82	F	CN	$N(SO_2C_2H_5)_2$	CH ₃	CF ₃	H
83	F	CN	N(CH ₃)SO ₂ CH ₃	CH ₃	CF ₃	Н
84	F	CN	N(CH ₃)SO ₂ C ₂ H ₅	CH ₃	CF ₃	Н
85	F	CSNH ₂	N(SO ₂ CH ₃) ₂	CH ₃	CF ₃	Н
86	F	CSNH ₂	N(SO ₂ C ₂ H ₅) ₂	CH ₃	CF ₃	Н
87	F	CN	SCH ₂ COOCH ₃	CH ₃	CF ₃	Н
88	F	CN	SCH ₂ COOC ₂ H ₅	CH ₃	CF ₃	H
89	F	CF ₃	NHSO ₂ CH ₃	CH ₃	CF ₃	Н
90	F	CF ₃	NHSO ₂ C ₂ H ₅	CH ₃	CF ₃	Н
91	F	CF ₃	OCH ₂ CH=CH ₂	CH ₃	CF ₃	Н
92	F	CF ₃	OCH2C≒CH	CH ₃	CF ₃	Н
93	F	CF ₃	OCH ₂ COOC ₅ H ₁₁	CH ₃	CF ₃	Н
94	F	CSNH ₂	N(CH ₃)SO ₂ CH ₃	CH ₃	CF ₃	Н



Ex.						
No.	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶
95	F	CSNH ₂	N(CH ₃)SO ₂ C ₂ H ₅	CH ₃	CF ₃	H
96	F	CSNH ₂	N(SO ₂ CH ₃) ₂	CH ₃	CF ₃	Н
97	F	CSNH ₂	N(SO ₂ C ₂ H ₅) ₂	CH ₃	CF ₃	Н
98	F	CN	OCH ₂ CH=CH ₂	H	CF₃	CH ₃
99	F	CN	OCH ₂ C≡CH	Н	CF ₃	СН3
100	F	CN	OCH(CH ₃)C≡CH	Н	CF ₃	CH ₃
101	F	CN	OCH ₂ COOCH ₃	Н	CF ₃	CH ₃
102	F	CN	OCH ₂ COOC ₂ H ₅	Н	CF ₃	CH ₃
103	F	CN	OCH ₂ COOCH(CH ₃) ₂	Н	CF ₃	CH ₃
104	F	CN	OCH2COOC5H11	Н	CF ₃	CH ₃
105	F	CN	OCH(CH ₃)COOC ₂ H ₅	Н	CF ₃	CH ₃
106	F	CN	NHSO ₂ CH ₃	Н	CF ₃	СН
107	F	CN	NHSO ₂ C ₂ H ₅	H	CF ₃	CH ₃
108	F	CN	NHSO ₂ CH ₂ Cl	Н	CF ₃	CH ₃
109	F	CN	NHSO ₂ CF ₃	Н	CF ₃	CH ₃
110	F	CSNH ₂	NHSO ₂ CH ₃	Н	CF ₃	CH ₃
111	F	CSNH ₂	NHSO₂C₂H5	Н	CF ₃	CH ₃
112	F	CN	Н	Н	CF ₃	Н
113	F	CSNH ₂	Н	Н	CF ₃	Н
114	F	CN	Н	CH ₃	CF ₃	Н
115	F	CSNH ₂	Н	CH ₃	CF ₃	Н
116	Н	CN	F	Н	CF ₃	Н
117	Н	CSNH ₂	F	Н	CF ₃	Н
118	Н	CN	F	CH ₃	CF ₃	Н
119	Н	CSNH ₂	F	CH ₃	CF ₃	Н
120	F	CSNH ₂	F	CH ₃	CF ₃	Н



Ex.	$\overline{}$	Γ		Γ		<u> </u>
No.	R¹	R²	R³	R ⁴	R ⁵	R ⁶
121	F	CN	H ₃ C SO ₂	CH ₃	CF ₃	Н
122	F	CN	H ₅ C ₂ SO ₂	СН₃	CF ₃	Н
123	F	CN	CH ₃ SO ₂ N H ₅ C ₂ SO ₂	СН3	CF ₃	н
124	F	CN	H _s C ₂ SO ₂	СН₃	CF₃	Н
125	F	CN	H ₅ C ₂	СН3	CF ₃	Н
126	F	CN	N N SO ₂ CI	CH₃	CF ₃	Н
127	F	CN	H ₃ C ₂ SO ₂ CI	СН3	CF ₃ .	Н



Ex.						
No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
128	F	CN	H ₅ C ₂ SO ₂	СН3	CF ₃	Н
129	F	CN	NHSO₂C₂H₅	CH ₃	CF ₃	CH ₃
130	F	CONH ₂	OCH ₃	CH ₃	CF ₃	Н
131	F	CN	OCH(CH ₃)COOCH(CH ₃) ₂	CH ₃	CF ₃	Н
132	F	CN	OCH(C ₂ H ₅)COOCH(CH ₃) ₂	CH ₃	CF ₃	Н
133	F	CN	NHSO₂CH3	CH ₃	CF ₃	COOC ₂ H ₅
134	F	CN	NHSO ₂ C ₂ H ₅	CH ₃	CF ₃	COOC ₂ H ₅
135	F	CN	OCH(C ₂ H ₅)COOCH ₃	CH ₃	CF ₃	Н
136	F	CN	OCH(C ₂ H ₅)COOC ₂ H ₅	CH ₃	CF ₃	Н
137	F	CN	OCH(CH ₃)COOCH ₃	CH ₃	CF ₃	Н
138	F	CN	OCH₂CN	CH ₃	CF ₃	H
139	F	CN	°~~	Н	CF ₃	Н
140	F	CN	°~~	СН3	CF ₃	н
141	F	CN	°~~	н	CF ₃	CH ₃
142	F	CN	· ~ ~	СН3	CF ₃	CH ₃
143	F	CN	00	Н	CF ₃	Н
144	. F	CN	00	СН3	CF ₃	Н
145	F	CN	00	н	CF ₃	CH ₃



Ex. No.	R ^I	R ²	R³	R ⁴	R ⁵	R ⁶
146	F	CN	000	СН3	CF ₃	СН3
147	F	CN	• ^ _	н	CF ₃	н
148	F	CN	• ` ` `	СН3	CF ₃	Н
149	F	CN	$\bigcirc \bigcirc$	Н	CF ₃	СН₃
150	F	CN	· \	СН3	CF ₃	СН₃
151	F	CN	o Cl	Н	CF ₃	н
152	F	CN	° CI	СН3	CF ₃	Н
153	F	CN	o Ca	Н	CF ₃	СН₃
154	F	CN	° Ca	СН₃	CF ₃	СН₃
155	F,	CN		СН3	CF ₃	Н
156	F	CN		Н	CF ₃	Н
157	F	CN	0,00	Н	CF ₃	CH ₃

Ex. No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
158	F	CN	0,00	СН3	CF ₃	Н
159	F	CN	0,000	СН3	CF ₃	СН₃
160	F	CN		Н	CF₃	Н
161	F	CN		СН3	CF ₃	н
162	F	CN		Н	CF ₃	СН₃
163	F	CN		СН3	CF ₃	СН₃
164	F	CN	о о сн ₃	Н	CF ₃	н
165	F	CN	о о сн,	CH ₃	CF ₃	Н
166	F	CN	о о сн,	н	CF ₃	CH ₃
167	F	CN	. о сн,	CH ₃	CF ₃	CH ₃

Ex. No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
168	F	CN	O C ₂ H ₅	н	CF ₃	н
169	F	CN	O C ₂ H ₅	СН3	CF ₃	Н
170	F	CN	.0 C ₂ H ₈	н	CF ₃	СН₃
171	F	CN	O^C ₂ H ₅	СН3	CF ₃	СН₃
172	F	CN		Н	CF ₃	Н
173	F	CN		СН3	CF ₃	н
174	F	CN		Н	CF ₃	СН₃
175	F	CN	0 > 0	СН3	CF ₃	СН₃
176	F	CN		Н	CF ₃	Н
177	F	CN		СН3	CF ₃	Н
178	F	CN		Н	CF ₃	СН3
179	F	CN		СН₃	CF ₃	CH ₃

F.,						
Ex. No.	R ¹	R²	R³	R⁴	R ⁵	R ⁶
180	F	CN	\sim	Н	CF ₃	н
181	F	CN	°	СН₃	CF ₃	н
182	F	CN		н	CF ₃	СН₃
183	F	CN	°\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	СН	CF ₃	СН₃
184	F	CN	о сно	H	CF ₃	Н
185	F	CN	о сно	CH ₃	CF ₃	Н
186	F	CN	о_сно	Н	CF ₃	СН₃
187	F	CN	ОСНО	СН3	CF ₃	CH ₃
188	F	CN	o √ OH	Н	CF ₃	н
189	F	CN	о Дон	СН3	CF ₃	Н
190	F	CN	ОМОН	Н	CF ₃	СН3
191	F	CN	о Дон	CH₃	CF ₃	СН₃
192	F	CN	O CH ₃	Н	CF₃	н
193	F	CN	O CH ₃	СН₃	CF ₃	Н

Ex.						
No.	R ¹	R²	R ³	R ⁴	R ⁵	R ⁶
194	F	CN	O CH ₃	Н	CF3	СН₃
195	F	CN	O CH ₃	СН₃	CF ₃	СН₃
196	F	CN		Н	CF ₃	Н
197	F	CN		СН₃	CF ₃	H
198	F	CN		н	CF ₃	СН3
199	F	CN		СН3	CF ₃	СН3
200	F	CN		Н	CF₃	Н
201	F	CN		СН3	CF ₃	н
202	F	CN	٠٠٠	Н	CF ₃	СН3
203	F	CN		CH ₃	CF ₃	CH₃
204	F	CN	CH ₃	Н	CF ₃	CH ₃
205	F	CN	CH3	СН3	CF ₃	Н



<u></u>						
Ex. No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
206	F	CN	0 0 0 0 0	н	CF ₃	СН₃
207	F	CN	O CH3	СН₃	CF ₃	СН₃
208	F	CN	O CH ₃	н	CF ₃	Н
209	F	.CN	о сн,	СН₃	CF ₃	Н
210	F	CN	о Сн	н	CF ₃	СН₃
211	F	CN	о	CH₃	CF₃	СН₃
212	F	CN	O CH,	н	CF ₃	Н
213	F	CN	O CH,	СН₃	CF₃	Н
214	F	CN	CH ₃ CH ₃	н	CF₃	СН₃
215	F	CN	O CH,	CH₃	CF ₃	СН₃



Ex. No.	\mathbb{R}^1	R²	R³	R ⁴	R ⁵	R ⁶
216	F	CN	O CH(CH ₃)₂	н	CF₃	Н
217	F	CN	O CH(CH ₃)₂	СН₃	CF ₃	н
218	F	CN	O CH(CH,)2	Н	CF ₃	СН3
219	F	CN	O CH(CH₃)₂	СН₃	CF ₃	СН3
220	F	CN	o H	н	CF ₃	Н
221	F	CN		СН3	CF ₃	Н
222	F	CN		Н	CF ₃	СН₃
223	F	CN		СН₃	CF ₃	СН3
224	F	CN	O N N	н	CF ₃	н
225	F	CN	CH ₃	СН₃	CF ₃	н



Ex. No.	R ¹	R²	R³	R⁴	R ⁵	R ⁶
226	F	CN	O CH,	Н	CF ₃	СН₃
227	F	CN	O N N	СН₃	CF₃	СН₃
228	F	CN	O NH NH	Н	CF ₃	Н
229	F	CN	CH ₃	СН₃	CF ₃	Н
230	F	CN	O NH NH	Н	CF ₃	СН₃
231	F	CN	CH ₃	СН3	CF ₃	СН₃
232	F	CN	O N(CH ₃) ₂	н	CF ₃	Н
233	F	CN	O N(CH ₃) ₂	СН3	CF ₃	Н
334	F	CN	O N(CH ₃) ₂	Н	CF ₃	СН₃

Ex. No.	\mathbb{R}^1	R ²	R³	R ⁴	R ⁵	R ⁶
235	F	CN	O O N(CH ₃) ₂	СН₃	CF ₃	СН₃
236	F	CN	$0 \longrightarrow N(C_2H_5)_2$ CH_3	н	CF ₃	н
237	F	CN	$O \xrightarrow{O} N(C_2H_5)_2$ CH_3	CH ₃	CF ₃	Н
238	F	CN	$0 \bigvee_{CH_3}^{O} N(C_2H_5)_2$	Н	CF ₃	СН₃
239	F	CN	O N(C ₂ H ₅) ₂	СН	CF ₃	СН₃
240	F	CN	O CH ₃	Н	CF ₃	Н
241	F	CN	O H N	СН₃	CF₃	Н
242	F	CN	O N N	Н	CF ₃	CH ₃
243	F	CN	CH ₃	СН3	CF ₃	СН₃

Ex. No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
244	F	CN	O N OH	Н	CF ₃	Н
245	F	CN	O N OH	СН₃	CF₃	н
246	F	CN	O NH OH	н	CF₃	СН₃
247	F	CN	O TH OH	СН₃	CF ₃	СН₃
248	F	CN	O CH3	Н	CF ₃	Н
249	F	CN	O CH3	СН₃	CF₃	Н
250	F	CN	O CH,	Н	CF₃	СН₃
251	F	CN	O CH ₃	СН₃	CF₃	СН₃
252	F	CN	O N N	н	CF ₃	Н



						,
Ex. No.	R ¹	R²	R³	R ⁴	R ⁵	R ⁶
253	F	CN	O H3	СН₃	CF ₃	Н
254	F	CN	O ZH	Н	CF ₃	СН₃
255	F	CN	O CH3	СН₃	CF ₃	СН₃
256	F	CN	OC ₃ H ₇ -n	CH ₃	CF ₃	·H
257	F	CN	CI	СН₃	CF ₃	н
258	F	CN	O CH ₃	CH ₃	CF ₃	Н
259	F	CN		СН	CF ₃	н
260	F	CN	N_SO ₂ CH ₃	СН3	CF₃	Н
261	F	CN	OO_C ₂ H ₅	Н	CF₃	Н



The compound listed above in Table 1 as Example 10 can, for example, be prepared as follows:

5 2.0 g (6.1 mmol) of 2-(4-cyano-2-fluoro-5-methoxy-phenyl)-4-methyl-5-trifluoro-methyl-pyridazin-3-one in 100 ml of dichloromethane are admixed with 18.4 g (18.3 mmol) of boron tribromide (1 molar solution in dichloromethane), the mixture is stirred at 25°C for 16 hours, 150 ml of water are then added slowly and the organic phase is dried over sodium sulphate and concentrated using a rotary evaporator.

This gives 1.8 g (94% of theory) of 2-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 189°C.

The compound listed above in Table 1 as Example 11 can, for example, be prepared as follows:



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3.9 g (13.5 mmol) of 3,3,3-trifluoro-2-oxopropanal-1-(4-cyano-2-fluoro-5-methoxy-phenylhydrazone) in 150 ml of toluene are admixed with 7.0 g (19.3 mmol) of (1-ethoxycarbonyl-ethylidene)-triphenylphosphorane, and the mixture is stirred under argon at reflux temperature for 2 hours. After concentration using a rotary evaporator, the residue is recrystallized from isopropanol.

This gives 2.2 g (50% of theory) of 2-(4-cyano-2-fluoro-5-methoxy-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 178°C.

The compound listed above in Table 1 as <u>Example 13</u> can, for example, be prepared as follows:

3.8 g (8 mmol) of 2-(4-bromo-2-fluoro-5-isopropoxy-phenyl)-4-methyl-5-trifluoro-methyl-pyridazin-3-one are dissolved in 10 ml of N-methyl-pyrrolidone, admixed with 0.9 g (9.6 mmol) of copper(I) cyanide and heated under reduced pressure (0.1 mbar) at 90°C, with distillative removal of 2 ml of solvent. The mixture is then heated under atmospheric pressure (under argon) to 170°C and stirred at this temperature for 6 hours. After cooling to 20°C, the mixture is stirred with 100 ml of ethyl acetate, admixed with 10% strength ammonia solution and filtered. The filtrate is washed with water, dried with sodium sulphate and carefully concentrated under waterpump vacuum.

This gives 3.0 g (89% of theory) of 2-(4-cyano-2-fluoro-5-isopropoxy-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one as crude product (content: 85% according to HPLC).

For further purification, 2 g of this crude product are chromatographed over silica gel using dichloromethane. This gives the pure product (0.7 g, content: 97% according to EHPLC) of melting point 121°C.

The compound listed above in Table 1 as <u>Example 15</u> can, for example, be prepared as follows:

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0.6 g (1.9 mmol) of 2-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-methyl-5-trifluoro-methyl-pyridazin-3-one in 30 ml of N,N-dimethyl-formamide are stirred at 25°C with 0.4 g (3 mmol) of potassium carbonate and 0.31 g (2.1 mmol) of propargyl bromide (80% pure) for 60 minutes, and the mixture is then admixed with water and adjusted to pH 6 using conc. hydrochloric acid, and precipitated product is filtered off with suction, washed with water and dried. For purification, the product is recrystallized from isopropanol.

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This gives 0.3 g (44% of theory) of 2-(4-cyano-2-fluoro-5-propargyloxy-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 145°C.

The compound listed above in Table 1 as <u>Example 18</u> can, for example, be prepared as follows:



0.7 g (2.24 mmol) of 2-(4-cyano-2-fluoro-5-hydroxy-phenyl)-4-methyl-5-trifluoro-methyl-pyridazin-3-one in 30 ml of N,N-dimethyl-formamide are stirred at 25°C with 0.48 g (3.5 mmol) of potassium carbonate and 0.42 g (2.5 mmol) of ethyl bromoacetate for 60 minutes, the mixture is then admixed with water and adjusted to pH 6 using conc. hydrochloric acid, and precipitated product is filtered off with suction, washed with water and dried.

This gives 0.64 g (71% of theory) of 2-[4-cyano-5-(ethoxycarbonylmethoxy)-2-fluoro-phenyl]-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 95°C.

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The compound listed above in Table 1 as Example 41 can, for example, be prepared as follows:

5.5 g (15 mmol) of 3,3,3-trifluoro-2-oxo-propanal-1-(4-cyano-5-ethylsulphonyl-amino-2-fluoro-phenylhydrazone) in 100 ml of toluene are admixed with 8.2 g (22.5 mmol) of (1-ethoxycarbonyl-ethylidene)-triphenylphosphorane, and the mixture is stirred under argon at reflux temperature for 2 hours. After concentration using a rotary evaporator, the residue is chromatographed over silica gel using toluene/ethyl acetate 3:1.

This gives 3.6 g (59.5% of theory) of 2-(4-cyano-5-ethanesulphonamino-2-fluorophenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 198°C.

The compound listed above in Table I as Example 66 can, for example, be prepared as follows:

1.6 g (4 mmol) of 2-(4-cyano-5-ethylsulphonylamino-2-fluoro-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one are initially charged in 30 ml of pyridine and 12 ml of triethylamine and, at 60-70°C, hydrogen sulphide is introduced underneath the surface of the liquid for 90 minutes. After the reaction has ended, the mixture is flushed with nitrogen for 60 minutes, cooled to 25°C and stirred with ice-water, precipitated product is filtered off with suction and the residue is washed with water and dried.

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This gives 0.9 g (51% of theory) of 2-(2-fluoro-5-ethylsulphonylamino-4-thio-carbamoyl-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 88°C

15 The compound listed above in Table 1 as <u>Example 122</u> can, for example, be prepared as follows:

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1.2 g (3 mmol) of 2-(4-cyano-5-ethylsulphonylamino-2-fluoro-phenyl)-4-methyl-5-trifluoromethyl-pyridazin-3-one in 50 ml of acetonitrile are admixed with 0.6 g (6 mmol) of triethylamine and 0.77 g (6 mmol) of 3-chloro-propionyl chloride, and the mixture is stirred at 25°C for 12 hours. After concentration using a rotary

evaporator, the residue is stirred with water and acidified with conc. hydrochloric acid, and precipitated product is filtered off with suction, washed with water and dried.

This gives 1.1 g of (2-[5-(N-ethenylcarbonyl-N-ethylsulphonylamino)-4-cyano-2-fluoro-phenyl]-4-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 96°C.

The compound listed above in Table 1 as <u>Example 129</u> can, for example, be prepared as follows:

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1.22 g (3.2 mmol) of 1-[(4-cyano-5-methylsulphonylamino-2-fluoro-phenyl)-hydrazono]-3-ethoxycarbonyl-1-chloro-1,1-difluoro-propan-2-one in 50 ml of toluene are admixed with 1.74 g (4.8 mmol) of (1-ethoxycarbonyl-ethylidene)-triphenyl-phosphorane, and the mixture is stirred under argon at reflux temperature for 2 hours. After concentration using a rotary evaporator, the residue is chromatographed over silica gel using toluene/ethyl.acetate 3:1.

This gives 0.2 g (15% of theory) of 2-(4-cyano-5-ethanesulphonamino-2-fluoro-phenyl)-4,6-dimethyl-5-trifluoromethyl-pyridazin-3-one of melting point 191°C.

The compound listed above in Table 1 as <u>Example 107</u> can, for example, be prepared as follows:



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1.22 g (3.2 mmol) of 1-[(4-cyano-5-methylsulphonylamino-2-fluoro-phenyl)-hydrazono]-3-ethoxycarbonyl-1-chloro-1,1-difluoro-propan-2-one in 50 ml of toluene are admixed with 1.7 g (4.8 mmol) of (1-ethoxycarbonyl-methylidene)-triphenyl-phosphorane, and the mixture is stirred under argon at reflux temperature for 2 hours. After concentration using a rotary evaporator, the residue is chromatographed over silica gel using toluene/ethyl acetate 3:1.

This gives 0.2 g (15.5% of theory) of 2-(4-cyano-5-ethylsulphonylamino-2-fluoro-phenyl)-6-methyl-5-trifluoromethyl-pyridazin-3-one of melting point 143°C.

Physical data for compounds listed in Table 1 are listed in Table 1a below.

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Table 1a:

Table 1a.					
Ex. No.	Physical data				
10	m.p.: 189°C				
10	$\log.P = 2.27^{a}$				
11	m.p.: 178°C				
11	$log.P = 2.76^{a}$				
12	$\log P = 3.12^{a}$				
13	m.p.: 121°C				
13	$\log.P = 3.40^{a}$				
14	$\log P = 3.24^{\text{ n}}$				
	NMR(CDCl ₃): 2.44-2.45; 4.65-4.68; 7.46-7.49; 8.03 ppm				
15	m.p.: 145°C				
	$log.P = 2.92^{a}$				
18	m.p.: 95°C				
	$log.P = 3.04^{a}$				
21	m.p.: 118°C				
22	m.p.: 174°C				
23	$log.P = 2.41^{a}$				
24	m.p.: 140°C				
	$\log P = 2.76^{a}$				
40	m.p.: 202°C				
40	$log.P = 2.91^{a}$				
41	m.p.: 198°C				
	log.P = 2.42 a)				
46	m.p.: 174°C				
66	m.p.: 88°C				
~	$log.P = 2.44^{a}$				
84	m.p.: 98°C				
	$log.P = 2.68^{a}$				



Ex. No.	Physical data					
107	m.p.: 143°C log.P = 2.31 ^{a)}					
112	m.p.: 160°C					
120	m.p.: 183°C log.P = 2.43 a)					
121	m.p.: 149°C log.P = 2.70 a)					
122	m.p.: 95°C log.P = 2.89 ^{a)}					
123	m.p.: 220°C					
124	m.p.: 135°C log.P = 3.39 ^{a)}					
125	$\log P = 3.03^{\text{ a}}$					
126	m.p.: 165°C log.P = 3.29 a)					
127	m.p.: 116°C log.P = 2.97 a)					
128	m.p.: 131°C					
129	m.p.: 189°C log.P = 2.65 a)					
130	m.p.: 142°C log.P = 1.94 *)					
131	log.P = 3.62 a) -NMR(CDCl ₃): 1.17-1.19; 1.25-1.27; 1.70-1.72; 2.43; 4.72-4.78; 6.94-6.96; 7.99 ppm					
132	log.P = 3.93 a) NMR(CDCl ₃): 1.13-1.26; 2.04-2.13; 2.43; 4.56-4.60; 7.46-7.49 ppm					



Ex. No.	Physical data					
133	m.p.: 134°C					
134	m.p.: 60°C					
135	NMR(CDCl ₃): 2.43-2.44; 3.77; 4.61-4.63; 8.01 ppm					
136	NMR(CDCl ₃): 2.07-2.12; 2.43-2.44; 4.19-4.24; 7.46-7.49; 8.00 ppm					
137	NMR(CDCl ₃): 1.72-1.74; 2.36; 4.77-4.82; 7.47-7.50; 8.01 ppm					
138	NMR(CDCl ₃): 2.44-2.46; 4.93; 7.55-7.58; 8.05 ppm					
158	log.P = 3.51 NMR(CDCl ₃): 2.44-2.54; 5.03; 7.26; 8.03 ppm					
161	m.p.: 83°C log.P = 3.65					
256	m.p.: 97°C					
257	m.p.: 221°C log.P = 4.17					
258	log.P = 4.64 NMR(CDCl ₃):1.54-1.55; 1.99-2.09; 2.42-2.44;4.25-4.26; 6.91-6.93 ppm					
259	m.p.: 161°C log.P = 3.10					
260	log.P = 2.93 NMR(CDCl ₃): 1.49-1.54; 2.01; 2.44-2.46; - 4.51-4.52; 7.60-7.63; 8.05 ppm					
261	m.p.: log.P = 2.91					



The logP values given above in Table 1 were determined in accordance with EEC Directive 79/831 Annex V.A8 by HPLC (High Performance Liquid Chromatography) using a reverse-phase column (C 18). Temperature: 43°C.

- (a) Mobile phases for the determination in the acidic range: 0.1% aqueous phosphoric acid, acetonitrile; linear gradient from 10% acetonitrile to 90% acetonitrile the corresponding test results in Table 1 are labelled a.
- (b) Mobile phases for the determination in the neutral range: 0.01 molar aqueous 10 phosphate buffer solution, acetonitrile; linear gradient from 10% acetonitrile to 90% acetonitrile - the corresponding test results in Table 1 are labelled b).

Calibration was carried out using unbranched alkan-2-ones (having 3 to 16 carbon atoms) with known logP values (determination of the logP values by the retention times using linear interpolation between two successive alkanones).

The lambda max values were determined in the maxima of the chromatographic signals using the UV spectra from 200 nm to 400 nm.

Starting materials of the formula (IV):

Example (IV-1)

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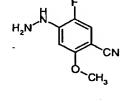
15

15 g (50 mmol) of 81% pure 4-cyano-2-fluoro-5-ethylsulphonylamino-aniline (known from DE-A-4414568) in a mixture with 100 ml of acetic acid and 20 ml of conc. sulphuric acid are cooled to 5°C and admixed a little at a time with 12.7 g (100 mmol) of nitrosylsulphuric acid, and the mixture is stirred at from 5°C to 10°C for 6 hours; a solution of 33.6 g (140 mmol) of tin(II) chloride dihydrate - dissolved in 15 ml of conc. hydrochloric acid - is then added dropwise at 10°C. The mixture is stirred at 25°C for 12 hours, then stirred with ice-water and made alkaline using conc. ammonia. The precipitated salt is filtered off with suction, the filtrate is made slightly acidic using conc. hydrochloric acid and extracted with ethyl acetate, and the extract is dried over sodium sulphate and concentrated using a rotary evaporator. The residue is recrystallized from isopropanol.

This gives 12.9 g (33% of theory) of 4-cyano-5-ethylsulphonylamino-2-fluoro-phenylhydrazine.

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Example (IV-1)





Step 1

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9.2 g (0.4 mol) of sodium metal are dissolved in 200 ml of methanol, and the solution is admixed with 30.8 g (0.2 mol) of 2,5-difluoro-4-cyano-aniline. The stirring apparatus is fitted with a distillation head and heated to 90-95°C, and about 4/5 of the amount of metanol is distilled off. After an extra stirring time of 30 minutes at 95°C, heating is removed, the content of the flask is admixed with water, cooled to 25°C and adjusted to pH 5 using conc. hydrochloric acid, and precipitated product is filtered off with suction, washed with water and dried.

This gives 31.2 g (94% of theory) of 4-cyano-2-fluoro-5-methoxy-aniline of melting point 99°C, purity (method): 99% (HPLC, logP 1.34).

Step 2 - Variant a

4.7 g (2.8 mmol) of 4-cyano-2-fluoro-5-methoxy-aniline are admixed with 100 ml of conc. hydrochloric acid and 30 ml of water, and the mixture is briefly heated to 40°C and then cooled to 0°C. A solution of 2.6 g of sodium nitrite - dissolved in 30 ml of water - is then added dropwise, and the mixture is stirred at from 5°C to 10°C for 60 minutes. The mixture is then filtered and the filtrate is, at 0°C, added dropwise to a solution of 18 g (8 mmol) of tin(II) chloride dihydrate in 100 ml of conc.



hydrochloric acid. The suspension is then stirred at room temperature (20°C) for 60 minutes, made alkaline using 45% strength aqueous sodium hydroxide solution and extracted repeatedly with ethyl acetate. The organic phase is dried over sodium sulphate and concentrated under waterpump vacuum using a rotary evaporator.

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This gives 3 g (60% of theory) of 4-cyano-2-fluoro-5-methoxy-phenylhydrazine of melting point 160°C.

Step 2 - Variant b

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20 g (0.5 mol) of sodium metal are dissolved in 400 ml of methanol, and the solution is admixed with 68 g (0.4 mol) of 2,5-difluoro-4-cyano-phenylhydrazine. The stirring apparatus is fitted with a distillation head and heated at from 80°C to 85°C, and about 80% of the methanol are distilled off. After an extra stirring time of 3 hours at 85°C, heating is removed, the content of the flask is admixed with water, cooled to 25°C and neutralized using conc. hydrochloric acid, and precipitated product is filtered off with suction, washed with water and dried. For purification, the product is recrystallized from ethanol.

This gives 39 g (54% of theory) of 4-cyano-2-fluoro-5-methoxy-phenylhydrazine of melting point 163°C.



Starting materials of the formula (VII):

Example (VII-1)

30 g (370 mmol) of sodium acetate are initially charged in 200 ml of water. With ice-cooling, 25 g (93 mmol) of 1,1-dibromo-3,3,3-trifluoroacetone are added dropwise, and the mixture is stirred at room temperature (about 20°C) for 30 minutes. The reaction mixture is then admixed with 12 g (72 mmol) of 2,5-difluoro-4-cyano-phenylhydrazine and stirred at from 40°C to 50°C for 2 hours. The cold precipitated product is filtered off with suction, washed with water and dried.

This gives 19 g (95.4% of theory) of 3,3,3-trifluoro-2-oxopropanal-1-(2,5-difluoro-4-cyano-phenylhydrazone) of melting point 181°C.

15 Example (VII-2)

7 g (87 mmol) of sodium acetate in 100 ml of water are admixed with 5.94 g (22 mmol) of 1,1-dibromo-3,3,3-trifluoro-acetone, and the mixture is stirred at room temperature (about 20°C) for 30 minutes, admixed with 3.0 g (17 mmol) of 4-cyano-2-fluoro-5-methoxy-phenylhydrazine and stirred at from 40°C to 50°C for 60 minutes and at 95°C for 10 minutes. After cooling to 20°C, the precipitated product is filtered off with suction, washed with water and dried.



This gives 4.1 g (83% of theory) of 3,3,3-trifluoro-2-oxo-propanal-1-(4-cyano-2-fluoro-5-methoxy-phenylhydrazone) of melting point 168°C.

Example (VII-3)

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4.1 g (50 mmol) of sodium acetate in 50 ml of water are stirred at 80°C with 3.6 g of 1,1-dibromo-3,3,3-trifluoro-acetone, the mixture is admixed at 25°C with 2.58 g (10 mmol) of 4-cyano-5-ethylsulphonylamino-2-fluoro-phenylhydrazine, stirred at from 40°C to 50°C for 90 minutes and cooled to 10°C, and precipitated product is filtered off with suction, washed with water and dried.

This gives 3.03 g (83% of theory) of 3,3,3-trifluoro-2-oxopropanal-1-(4-cyano-5ethylsulphonylamino-2-fluoro-phenylhydrazone) of melting point 127°C.

Example (VII-4)



4.1 g (50 mmol) of sodium acetate in 50 ml of water are stirred at 80°C with 3.6 g of 3,3-dibromo-1,1,1-trifluoro-2-butanone for 30 minutes, and the mixture is admixed at 25°C with 2.58 g (10 mmol) of 4-cyano-5-ethylsulphonylamino-2-fluoro-phenyl-

hydrazine, stirred at from 40°C to 50°C for 2 hours and cooled to 10°C. The precipitated product is filtered off with suction, washed with water and dried.

This gives 3.2 g (84.2% of theory) of 1,1,1-trifluoro-2-oxo-butanal-3-(4-cyano-5-ethylsulphonylamino-2-fluoro-phenylhydrazone) of melting point 211°C.

Precursors of the formula (XIV):

Example (XIV-1)

F₃C-CF₂ N- N- CN
H₃C-SO₂ NH

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6.87 g (30 mmol) of 4-cyano-5-methylsulphonylamino-2-fluoro-aniline are initially charged in 100 ml of acetic acid, 4.7 g (34 mmol) of nitrosylsulphuric acid (92% strength) are introduced a little at a time at 20°C with ice-cooling, and the mixture is stirred at 25°C for 2 hours. At 5-10°C, the mixture is subsequently added dropwise to a suspension of 10.6 g (45 mmol) of ethyl pentafluoropropinylacetate and 16.4 g (200 mmol) of sodium acetate in 200 ml of ethanol, the mixture is stirred at 25°C for 12 hours and stirred into water, and precipitated product is filtered off with suction, washed with water and dried. For purification, the product is recrystallized from isopropanol.

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This gives 8.6 g (60.5% of theory) of 1-[(4-cyano-5-methylsulphonylamino-2-fluoro-phenyl)hydrazono]-4-ethoxycarbonyl-1,1,1,2,2-pentafluorobutan-3-one of melting point 165°C.



Example (XIV-2)

10.7 g (47 mmol) of 4-cyano-5-methylsulphonylamino-2-fluoro-aniline are initially charged in 100 ml of acetic acid, 7.3 g (53 mmol) of nitrosylsulphuric acid (92% strength) are introduced at 20°C a little at a time with ice-cooling, and the mixture is stirred at 25°C for 2 hours. At from 5°C to 10°C, the mixture is then added dropwise to a suspension of 14.2 g (71 mmol) of ethyl 1,1,1-difluorochloroacetoacetate and 26 g (313 mmol) of sodium acetate in 200 ml of ethanol, the mixture is stirred at 25°C for 12 hours and stirred into water, and precipitated product is filtered off with suction, washed with water and dried.

This gives 13.7 g (66% of theory) of 1-[(4-cyano-5-methylsulphonylamino-2-fluoro-phenyl)hydrazono]-3-ethoxycarbonyl-1,1-difluoro-1-chloro-propan-2-one of melting point 175°C.



Use Examples:

In the use examples, the following known compounds are used for comparison:

$$H_3C$$
 N
 CI
 NH_2
 (A)

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2-(5-amino-2,4-dichloro-phenyl)-5-methyl-3(2H)-pyridazinone

- known from WO 9639392.

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4-bromo-2-(2,4-dichloro-5-nitro-phenyl)-5-methyl-3(2H)-pyridazinone

- known from WO 9639392.

(C)

2-(5-amino-2,4-dichloro-phenyl)-4-bromo-5-methyl-3(2H)-pyridazinone

- known from WO 9639392.

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 $\hbox{2--}(2,4-dichloro-5-nitro-phenyl)-5-methyl-3 (2H)-pyridazinone$

- known from WO 9639392.

2,5-difluoro-4-(4-methyl-6-oxo-1(6H)-pyridazinyl)-benzonitrile

- known from WO 9639392.



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Example A

Pre-emergence test

5 . Solvent:

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5 parts by weight of acetone

Emulsifier:

I part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, I part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

Seeds of the test plants are sown in normal soil. After about 24 hours, the soil is sprayed with the preparation of active compound such that the particular amount of active compound desired is applied per unit area. The concentration of the spray liquor is chosen so that the particular amount of active compound desired is applied in 1000 litres of water per hectare.

After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control.

The figures denote:

0% =

no effect (like untreated control)

100% =

total destruction

25

In this test, for example, the compounds of Preparation Example 1, 2, 12, 13, 24, 40, 46, 66, 84, 107, 112, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129 and 133 show considerably stronger activity against weeds than the known compounds (A), (B),(J), (D) and (E).

Example B

Post-emergence test

5 Solvent: 5

5 parts by weight of acetone

Emulsifier:

1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

Test plants of a height of 5-15 cm are sprayed with the preparation of active compound such that the particular amounts of active compound desired are applied per unit area. The concentration of the spray liquor is chosen so that the particular amounts of active compound desired are applied in 1000 l of water/ha.

After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control.

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The figures denote:

0% = no effect (like untreated control)

100% = total destruction

In this test, for example, the compounds of Preparation Example 1, 2, 12, 13, 24, 40, 41, 46, 66, 84, 107, 112, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129 and 133 show considerably stronger activity against weeds than the known compounds (A), (B), (C), (D) and (E).



Example C

Phaedon larvae test

5 Solvent:

7 parts by weight of dimethylformamide

Emulsifier:

1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, I part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

Cabbage leaves (Brassica oleracea) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with mustard beetle larvae (Phaedon cochleariae) while the leaves are still moist.

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Ç.

After the desired period of time, the kill in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

20 In this test, for example, the compounds of Preparation Examples 1 and 2 show good activity.

Note: Amendments have been made to the claims which appear hereafter in order to further define the invention. These amendments are based on preferments of the various groups of the compounds described herein. For integrity of the text, and of the specification as filed, corresponding amendments have not been made to the statement of invention which appears on pages 1 to 4.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge in Australia.



The claims defining the invention are as follows:

1. Substituted phenylpyridazinones of the general formula (I)

in which

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R1 represents hydrogen, fluorine or chlorine,

R² represents cyano or thiocarbamoyl,

R³ represents the grouping -A¹-A²-A³ in which

A¹ represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, methyl, ethyl, n- or i-propyl, methyl-sulphonyl or ethylsulphonyl,

A1 furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, ethene-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,

A². represents a single bond, represents oxygen, sulphur, -SO-, -SO₂-, -CO- or the grouping -N-A⁴-, in which A⁴ represents hydrogen, methyl, ethyl, n- or i-propyl,

methoxy, ethoxy, n- or i-propoxy, methylsulphonyl, ethylsulphonyl, n- or i-propyl sulphonyl or phenylsulphonyl,

A² furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,

represents hydrogen, hydroxyl, amino, cyano, nitro, carboxyl, carbamoyl, sulpho, fluorine, chlorine, bromine, represents in each case unsubstituted or fluorine-, chlorine-, methoxy- or ethoxy substituted methyl, ethyl, nor i-propyl, n-, i-, s- or t-butyl, n-, i-, s- or t-pentyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, n-, i-, s- or t-pentyloxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylsulphinyl, ethylsulphinyl, n- or i-propylsulphinyl, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl, methylamino, ethylamino, nor i-propylamino, n-, i-, s- or t-butylamino, dimethylamino, diethylamino, methoxycarbonyl, ethoxycarbonyl, n- or ipropoxycarbonyl, represents in each case unsubstituted or fluorine or chlorine-substituted propenyl, butenyl, propenyloxy, butenyloxy, propenylamino, butenylamino, propylideneamino, butylideneamino, propenyloxycarbonyl, butenyloxycarbonyl, propinyl, butinyl, propinyloxy, butinyloxy, propinylamino, butinylamino, propinyloxycarbonyl or butinyloxycarbonyl, represents in each case unsubstituted or fluorine-, chlorine-, cyano-, carboxyl-, methyl-, ethyl-, n- or i-propyl-, methoxycarbonyl- or ethoxycarbonyl-substituted cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, cyclopropyl-

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A³

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methoxy, cyclobutylmethoxy, cyclopentylmethoxy, cyclohexylmethoxy, cyclopentylideneamino, cyclohexylideneamino, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, cyclopentylmethoxycarbonyl or cyclohexylmethoxycarbonyl, or represents in each case unsubstituted or nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy, trifluoromethoxy-, methoxycarbonyl- and/or ethoxycarbonyl-substituted phenyl, phenyloxy, benzyl, phenylethyl, benzyloxy, phenyloxycarbonyl or benzyloxycarbonyl,

A3 furthermore represents pyrazolyl, imidazolyl, triazolyl, furyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolylmethyl, furylmethyl, thienylmethyl, oxazolylmethyl, isoxazolemethyl, thiazolemethyl, pyridinylmethyl, pyrimidinylmethyl, pyrazolylmethoxy, furylmethoxy or pyridylmethoxy,

R4 represents hydrogen or methyl,

represents trifluoromethyl, and

represents hydrogen, cyano, thiocarbamoyl, nitro, fluorine, chlorine, bromine, or represents in each case unsubstituted or fluorine-and/or chlorine-substituted methyl, ethyl, n- or i-propyl, methoxy, ethoxy, methylthio, ethylthio, methylamino, ethylamino, dimethylamino, methoxycarbonyl or ethoxycarbonyl.

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R⁵

K_e



		2.	Substituted phenylpyridazinones according to claim 1, in which			
			R ¹	represe	ents fluorine,	
	5		R ²	repres	ents cyano or thiocarbamoyl,	
			R ³	repres	ents the grouping -A ¹ -A ² -A ³	
	10			A ¹	represents a single bond, represents oxygen, sulphur, -SO-, -SO ₂ -, -CO- or the grouping -N-A ⁴ -, in which A ⁴ represents hydrogen, methyl, ethyl, n- or i-propyl, methyl-sulphonyl or ethylsulphonyl,	
	15			A ¹	furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,	
	20			A ²	represents a single bond, represents oxygen, sulphur, -SO-, -SO ₂ -, -CO- or the grouping -N-A ⁴ -, in which A ⁴ represents hydrogen, methyl, ethyl, n- or i-propyl, methoxy, ethoxy, n- or i-propoxy, methylsulphonyl, ethylsulphonyl, n- or i-propyl sulphonyl or phenylsulphonyl,	
	25			A ²	furthermore represents methylene, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,2-diyl, propene-1,2-diyl or propene-1,3-diyl,	
	30	OFFIC	THE PARTY OF THE P	A ³	represents hydrogen, hydroxyl, amino, cyano, nitro, carboxyl, carbamoyl, sulpho, fluorine, chlorine, bromine, represents in each case unsubstituted or fluorine-,	

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chlorine-, methoxy- or ethoxy substituted methyl, ethyl, nor i-propyl, n-, i-, s- or t-butyl, n-, i-, s- or t-pentyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, n-, i-, s- or t-pentyloxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylsulphinyl, ethylsulphinyl, n- or i-propylsulphinyl, methylsulphonyl, ethylsulphonyl, n- or i-propylsulphonyl, methylamino, ethylamino, nor i-propylamino, n-, i-, s- or t-butylamino, dimethylamino, diethylamino, methoxycarbonyl, ethoxycarbonyl, n- or ipropoxycarbonyl, represents in each case unsubstituted or fluorine or chlorine-substituted propenyl, butenyl, propenyloxy, butenyloxy, propenylamino, butenylamino, propylideneamino, butylideneamino, propenyloxycarbonyl, butenyloxycarbonyl, propinyl, butinyl, propinyloxy, butinyloxy, propinylamino, butinylamino, propinyloxycarbonyl or butinyloxycarbonyl, represents in each case unsubstituted or fluorine-, chlorine-, cyano-, carboxyl-, methyl-, ethyl-, n- or i-propyl-, methoxycarbonyl- or ethoxycarbonyl-substituted cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, cyclopropylmethyl, cyclobutylmethyl, cyclopentylmethyl, cyclohexylmethyl, cyclopropylmethoxy, cyclobutylmethoxy, cyclopentylmethoxy, cyclohexylmethoxy, cyclopentylideneamino, cyclohexylideneamino, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, cyclopentylmethoxycarbonyl or cyclohexylmethoxycarbonyl, or represents in each case unsubstituted or nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy, trifluoromethoxy-, methoxycarbonyl- and/or ethoxycarbonyl-substituted phenyl, phenyloxy, benzyl, phenylethyl, benzyloxy, phenyloxycarbonyl or benzyloxycarbonyl,

R4 represents hydrogen or methyl, R5 represents trifluoromethyl, and 5 represents hydrogen, methyl or ethoxycarbonyl. R6 Substituted phenylpyridazinones according to Claim 1, characterized 3. in that R1 represents fluorine. 10 Substituted phenylpyridazinones according to any of Claims 1 or 2, 4. 1 characterized in that R2 represents cyano. Substituted phenylpyridazinones according to any of Claims 1 or 2, 5. characterized in that R1 represents fluorine and R2 represents cyano. 15 Substituted phenylpyridazinones according to Claim 5, characterized 6. in that R4 and R6 represent hydrogen or methyl... Substituted phenylpyridazinones according to Claim 6, characterized 20 7. in that R³ represents A³. Substituted phenylpyridazinones according to Claim 6, characterized 8. in that A1 represents -NH- and A2 represents SO2. 25 Substituted phenylpyridazinones according to Claim 6, characterized 9. in that A1 represents methylsulphonyl or ethylsulphonyl and A2 represents -CO-. Process for preparing substituted phenylpyridazinones according to 30 10. any of Claims 1 to 9, characterized in that halogenoarenes of the general formula (II) (a)

$$X^1$$
 R^3
(III)

in which

 R^1 , R^2 and R^3 are as defined in any of Claims 1 or 2 and X^1 represents halogen

are reacted with pyridazinones of the general formula (III)

in which

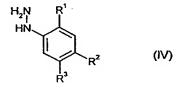
 $R^4,\,R^5$ and R^6 are as defined in any of Claims 1 or 2,

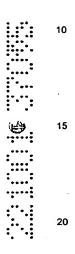
or with acid adducts or alkali metal salts of compounds of the formula (III)

if appropriate in the presence of a reaction auxiliary and if appropriate in the presence of a diluent,

or that

(b) arythydrazines of the general formula (IV)







in which

 $\ensuremath{R^1}\xspace, \ensuremath{R^2}\xspace$ and $\ensuremath{R^3}\xspace$ are as defined in any of Claims 1 or 2

are reacted with ß-trihalomethyl-enones of the general formula

in which

R4, R5 and R6 are as defined in any of Claims 1 or 2 and X2 represents halogen,

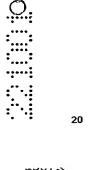
if appropriate in the presence of a reaction auxiliary and if appropriate in the presence of a diluent,

or that

(c) hydrazonecarboxylic acids of the general formula (VI)

in which

R¹, R², R³, R⁴, R⁵ and R⁶ are as defined in any of Claims 1or 2 are condensed with ring-closure, i.e. reacted with a dehydrating agent,



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or that

(d) 2,4-disubstituted phenylpyridazinones of the general formula (la)

$$R^5$$
 R^6
 R^7
 R^4
 R^4
 R^2
(Ia)

in which

 ${\sf R}^1, {\sf R}^2, {\sf R}^4, {\sf R}^5$ and ${\sf R}^6$ are as defined in any of Claims 1 or 2,

are nitrated, i. e. reacted with a nitrating agent,

or that

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(e) hydrazonecarbonyl compounds of the general formula (VII)

in which

, R1, R2, R3, R5 and R6 are as defined in any of Claims 1 or 2

reacted with alkoxycarbonylmethylenephosphoranes of the general formula (VIII)

$$CO_2R$$
 $P(C_6H_5)_3$
(VIII)

in which



R4 is as defined in any of Claims 1 or 2 and

R represents alkyl having 1 to 6 carbon atoms,

or with trialkyl phosphonocarboxylates of the general formula (IX)

$$CO_2R$$
 $PO(OR)_2$
(IX)

in which

R4 is as defined in any of Claims 1 or 2 and

R represents alkyl having 1 to 6 carbon atoms,

in each case optionally in the presence of a reaction auxiliary and optionally in the presence of a diluent.

15 11. Hydrazonecarbonyl compounds of the general formula (VIIa)

in which

R1 represents fluorine, chlorine or bromine,

R2-1 represents cyano, carbamoyl, thiocarbamoyl, or represents in each case unsubstituted or fluorine- and/or chlorine-substituted alkyl, alkoxy or alkylthio having in each case 1 or 2 carbon atoms,

R³ represents the grouping -A¹-A²-A³. in which



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represents a single bond, represents oxygen, sulphur, Α¹ -SO-, -SO2-, -CO- or the grouping -N-A4-, in which A4 represents hydrogen, hydroxyl, C₁-C₄-alkyl, C₃-C₄alkenyl, C3-C4-alkinyl, C1-C4-alkoxy, phenyl, C1-C4-alkyl-5 sulphonyl or phenylsulphonyl, furthermore represents in each case unsubstituted or Α1 fluorine-, chlorine- or bromine-substituted C1-C6-alkanediyl, C₂-C₆-alkenediyl, C₂-C₆-azaalkenediyl, C₂-C₆-alki-10 nediyl, C₃-C₆-cycloalkanediyl, C₃-C₆-cycloalkenediyl or O phenylene, represents a single bond, represents oxygen, sulphur, A² -SO-, -SO₂₇, -CO- or the grouping -N-A₄₇, in which A₄ 15 represents hydrogen, hydroxyl, C1-C4-alkyl, C1-C4alkoxy, phenyl, C₁-C₄-alkylsulphonyl or phenylsulphonyl, furthermore represents in each case unsubstituted or A^2 fluorine- chlorine- or bromine-substituted C₁-C₆-20 alkanediyl, C_2 - C_6 -alkenediyl, C_2 - C_6 -azaalkenediyl, C_2 - C_6 -alkinediyl, C_3 - C_6 cycloalkanediyl, C_3 - C_6 -cycloalkenedivl or phenylene, represents hydrogen, hydroxyl, amino, cyano, isocyano, Α³ thio cyanato, nitro, carboxyl, carbamoyl, thiocarbamoyl, 25

sulpho, chlorosulphonyl, fluorine, chlorine, bromine, represents in each case unsubstituted or fluorine, chlorine- or C₁-C₄-alkoxy substituted alkyl, alkoxy, alkylthio, alkylsulphinyl, alkylsulphonyl, alkylamino, dialkylamino, alkoxycarbonyl or dialkoxy(thio)phosphoryl having in each case 1 to 6 carbon atoms in the alkyl groups, represents in each case unsubstituted or fluorine- or

chlorine-substituted alkenyl, alkenyloxy, alkenylamino, alkylideneamino, alkenyloxycarbonyl, alkinyl, alkinyloxy, alkinylamino or alkinyloxycarbonyl having in each case 2 to 6 carbon atoms in the alkenyl, alkylidene or alkinyl groups, represents in each case unsubstituted or fluorine-, chlorine-, cyano-, carboxyl-, C1-C4-alkyl and/or C₁-C₄-alkoxy-carbonyl substituted cycloalkyl, cycloalkyloxy, cycloalkylalkyl, cycloalkylalkoxy, cycloalkylideneamino, cycloalkyloxycarbonyl or cycloalkylalkoxycarbonyl having in each case 3 to 6 carbon atoms in the cycloalkyl groups and unsubstituted or 1 to 4 carbon atoms in the alkyl groups, or represents in each case unsubstituted or nitro-, cyano-, carboxyl-, fluorine-, chlorine-, bromine-, C₁-C₄-alkyl-, C₁-C₄-halogenoalkyl-, C₁-C₄-alkyloxy-, C₁-C₄-halogenoalkyloxy- and/or C₁-C₄-alkoxy-carbonyl-substituted phenyl, phenyloxy, phenyl-C1-C4-alkyl, phenyl-C₁-C₄-alkoxy, phenyloxycarbonyl or phenyl-C₁-C₄alkoxycarbonyl,

furthermore represents in each case unsubstituted or fully or partially hydrogenated pyrrolyl, pyrazolyl, imidazolyl, triazolyl, furyl, oxiranyl, oxetanyl, dioxolanyl, thienyl, oxazolyl, isoxazolyl, thiazolyl, isothiazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, triazinyl, pyrazolyl-C₁-C₄-alkyl, furyl-C₁-C₄-alkyl, thienyl-C₁-C₄-alkyl, oxazolyl-C₁-C₄-alkyl, isoxazole-C₁-C₄-alkyl, thiazole-C₁-C₄-alkyl, pyridinyl-C₁-C₄-alkyl, pyrimidinyl-C₁-C₄-alkyl, pyrazolyl-methoxy, furylmethoxy, represents perhydropyranyl-methoxy or pyridylmethoxy,

represents hydrogen, cyano, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in

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each case unsubstituted or fluorine- and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino or dialkylamino having in each case 1 to 4 carbon atoms in the alkyl groups, and

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represents hydrogen, cyano, thiocarbamoyl, nitro, hydroxyl, mercapto, amino, fluorine, chlorine, bromine, or represents in each case unsubstituted or fluorine- and/or chlorine-substituted alkyl, alkoxy, alkylthio, alkylamino or dialkylamino having in each case 1 to 4 carbon atoms in the alkyl groups.

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 Crop protection compositions, characterized in that they comprise at least one substituted phenylpyridazinone according to Claim 1 and customary extenders and/or surfactants.

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13. Method for controlling undesirable plants, characterized in that at least one substituted phenylpyridazinone according to Claim 1 is allowed to act on undesirable plants and/or their habitat.

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14. Method for controlling undesirable insects, characterized in that at least one substituted phenylpyridazinone according to Claim 1 is allowed to act on undesirable insects and/or their habitat.

15. Substituted phenylpyridazinones of the general formula (I), processes for their preparation, crop protection compositions or methods for controlling involving/containing them, substantially as hereinbefore described with reference to the Examples.

DATED this 28th day of September, 2001

BAYER AKTIENGESELLSCHAFT
By its Patent Attorneys
DAVIES COLLISON CAVE



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